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ASD INTERIM REPORT 7-648 (III)
January 1963

CHEMICAL COMPOUNDS FOR METAL SHAPING

J. L. Jamieson
E. G. Partridge
et al.

DOUGLAS AIRCRAFT COMPANY, INC.
(Aircraft Division)

Contract: AF33(600)-43027
ASD Project: 7-648

Interim Technical Progress Report
1 July 1962 - 31 December 1962

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MANUFACTURING TECHNOLOGY LABORATORY

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United States Air Force
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Acid loss by syneresis presently requires a gel aging period of four to ten days in closed containers before an accurate and smooth etch can be achieved.

In electrolytic chemical etching, polarization of the anodic workpiece was caused usually by deposit of insoluble reaction products, and in some cases deposit of soluble salts which left no visible film. Intermittent direct current, superimposed AC, and ultrasonic vibration failed to prevent this. The gel etchant was replenished with liquid etchant by positive flow and by partial immersion. Removal of reaction products improved, but a steady state process could not be maintained.

On plate stock, the electrochemical method failed to improve the rate and magnitude of etch with a single gel. Further study of mass diffusion through gels will be required to overcome the problem of removing reaction products.

The greatly improved etch rate of the electrochemical method on honeycomb, compares favorably with the rate of conventional liquid chemical milling for the same material. This is attributable to a proportionately greater volume of gel to absorb and disperse reaction products. The improvements noted after etching in a dielectric liquid were due to (1) control of acid evaporation losses and gel warpage, (2) prevention of acid vapor attack on exposed cell walls, (3) heat transfer through the liquid, and (4) better dispersal of reaction products.

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NOTICES

FOREWORD

This Interim Technical Progress Report covers the work performed under contract AF33(600)-43027 from 1 July 1962 to 31 December 1962. It is published for technical information only and does not necessarily represent the recommendations, conclusions, or approval of the Air Force.

This contract with Douglas Aircraft Company, Inc., Long Beach, California was initiated under ASD Manufacturing Technology Laboratory Project 7-648, "Chemical Compounds for Metal Shaping". It is administered under the direction of Mr. Elmer S. Smith of the Basic Industry Branch (ASRCTF), Manufacturing Technology Laboratory, ASC Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

Mr. J. L. Jamieson, Tool Engineer assigned to the Douglas Company's Tooling Research and Development Group (Aircraft Division) is the project engineer. Mr. W. H. Hyter, Research Chemical Engineer assigned to the Materials and Process Engineering Department serves as consultant. The chemical development portion of this project is being performed by the Chemical Engineering Department of the University of Southern California under sub-contract to the Douglas Aircraft Company. Mr. L. A. Holmes, Mr. D. R. Larson, and Mr. G. M. Mallan, of the university research staff are conducting the chemical research and development under the direction of Dr. F. J. Lockhart, head of the Department of Chemical Engineering, with faculty members Dr. J. R. Cady and Dr. E. G. Partridge serving as consultants.

The primary objective of the Air Force Manufacturing Methods Program is to increase producibility, and improve the quality and efficiency of fabrication of aircraft, missiles, and components thereof. This report is being disseminated in order that methods and/or equipment developed may be used throughout industry, thereby reducing costs and giving "MORE AIR FORCE PER DOLLAR".

Your comments are solicited on the potential utilization of the information contained herein as applied to your present or future production programs. Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

PUBLICATION REVIEW

Approved:

R J Nicholson

R. J. Nicholson, Tool Project Engineer
Tooling Research and Development

A K Beer

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Chief Tool Project Engineer

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INTRODUCTION

The first Interim Technical Progress Report, ASD TR 7-648 (I), published in January, 1962, discussed the advantages of developing solid or semi-solid etchants to supplement the conventional liquid chemical milling process. This report also discussed the necessity of expanding chemical milling applications and developing etchants for alloy steels and refractory metals. In the initial research phase, several gel etchant systems were prepared which had acid solutions suspended in a gel matrix of organic, water-soluble resins. This, in itself, was significant since gels are basically alkaline. These gel etchants were cast into semi-rigid shapes and successfully removed metal when placed in contact with the work surface. In the small scale operation, the reaction products and reactants were observed to migrate countercurrently through the gel as desired. In addition to the gel system development, there was a preliminary investigation of rigid, porous solid materials for delivery of liquid etchants and removal of reaction products.

As reported in the second Interim Technical Progress Report, ASD TR 7-648 (II), published in July, 1962, continued development improved the physical, chemical and mechanical properties of the gel systems. Gels were accurately cast with smooth surfaces and variable shear strengths for rough and finish etching. Reactants and reaction products diffused sufficiently through the gel to permit replenishment by adding fresh acid. Initial attempts to etch steel plate stock were only partially successful. Subsequent improvements are noted in this report. Chemical milling of stainless steel honeycomb with gel etchants showed considerable promise. Flat cuts and contoured cavities were etched with good dimensional control and with significant improvement in etch rate and surface quality. Other laboratory tests indicated that porous solids could be used as a contour matrix and carrier for liquid etchants, but that dimensional control and surface finish would require considerable improvement.

Work has continued during the past six month period with special emphasis on improving gel formulations and properties, and on a study of the effectiveness of electrical energy in improving the performance of both liquid and gel etchants. The present report covers the progress of this work to date.

The objective of this research is defined in detail by the first interim report. Although the approach is subject to modifications, as may be indicated by cumulative results, no change is contemplated in the ultimate objective. Briefly, the objective is to develop semi-solid etchants which can be cast or molded to a desired shape, or rolled to a desired thickness, and be capable of removing metal from alloy steels and refractory metals at economical rates and with dimensional tolerance and surface finish equal to, or better than that attainable by conventional liquid chemical milling.

SECTION I
DISCUSSION

A. THE GEL SYSTEMS

The effort previously reported in Interim Technical Progress Reports determined that acid etchants could be satisfactorily gelled and that the gels could etch steel plate stock and honeycomb core materials. It was also determined that etching of plate stock was severely limited by the amount of chemical energy available in the gel mass, by gas entrapment at the gel-workpiece interface, and by difficulty of removing reaction products in greater volumes than had been attempted in the initial experiments. Honeycomb core materials were similarly affected, but to a much lesser degree.

The principal effort during this reporting period was devoted to supplementing chemical energy with electrical energy. (Subsections B. through D. treat this area in detail.) However, continued development effort was directed toward basic problems of the two most feasible gels. These are acid gels employing cellulose acetate and carboxymethylcellulose as gelling agents. At this stage of the laboratory work, it was considered better to explore in detail the characteristics of one particular gel which appeared to have the most desirable properties instead of a more superficial study of a number of gels. Consequently, most of the work during this period was done with cellulose acetate gels. Although these require a longer gelation period (2-3 days) than the carboxymethylcellulose gels (15-20 minutes) due to gradual hydrolysis, the resulting gels were found to be more firm, less elastic, and to have good storage properties over a reasonable period of time.

Stratification became apparent in both gels, but the significance of this phenomenon has not been conclusively determined. Shortly after cellulose acetate was dispersed through the hydrochloric-nitric acid mixture, a visible horizontal separation was noted as gelation commenced simultaneously from the top and bottom of the vessel. (Experiment H-1*). In several cases, this resulted in diminishing liquid strata with entrapped gas bubbles (H-3). Figure 1 illustrates this separation approximately 60 minutes after blending the cellulose acetate and mixed acids. The upper 56% of the beaker and the lower 4% are already filled with the white gel, while a darker intermediate layer remains liquid with suspended gas bubbles. In some cases, gelation was incomplete with slight liquid strata remaining. In other cases, gelation was complete, but the resulting gels lacked uniformity.

In subsequent etching tests with plate stock, the migration or diffusion of reaction products appeared to be inhibited in the region where the liquid layer occurred during the gelation period.

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* Reference to experimental notes, Appendix D.

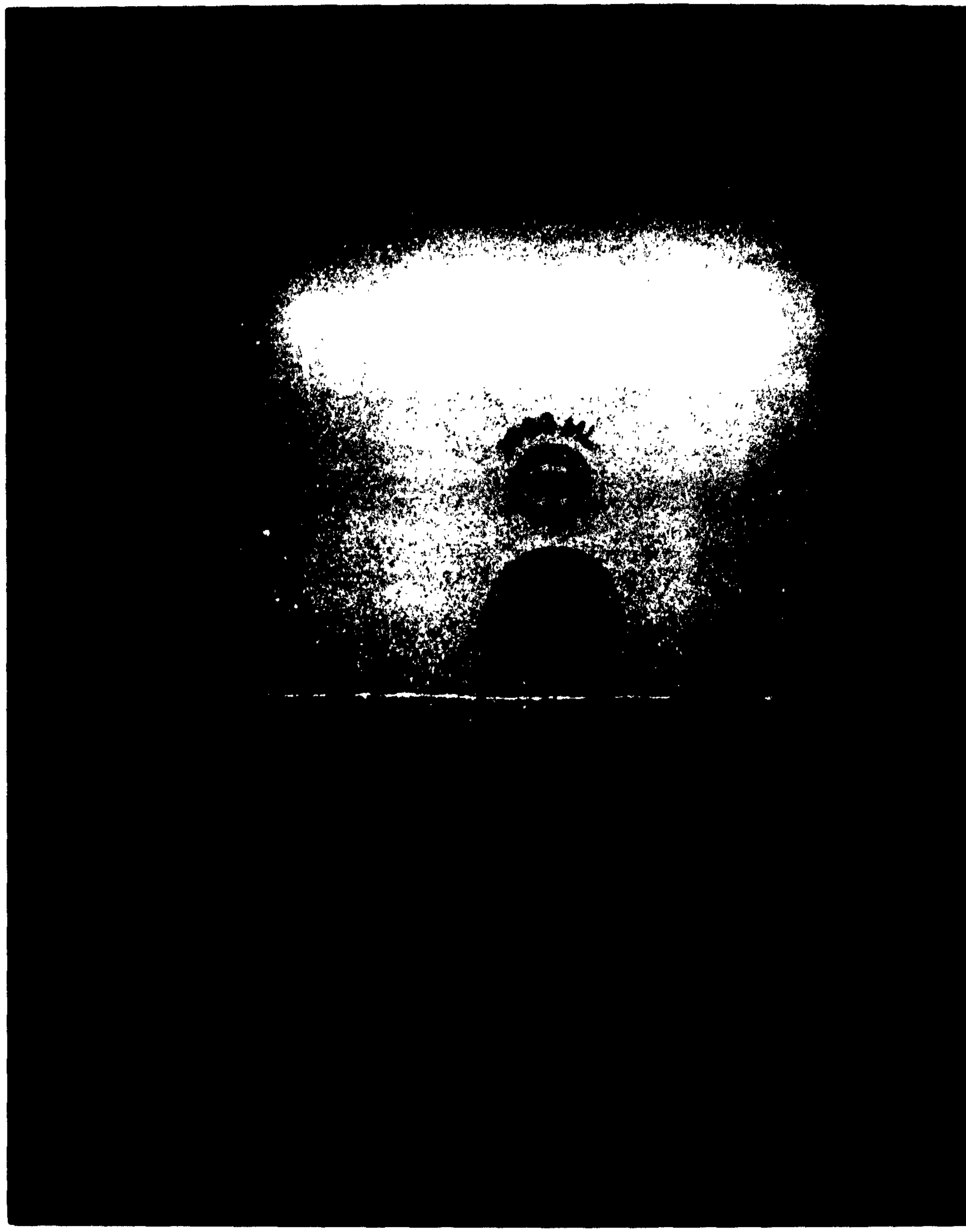


Figure 1 - Separation of cellulose acetate one hour after mixing in etching solution. Gelation begins from the top and bottom and continues until the two layers meet.

Attempts to reduce or prevent stratification by the addition of Polyox (polyethyleneoxide resin) or fluorocarbon latex (H-4, L-28) adversely affected the structural integrity of the gel. However, heating the mixture to the range of 110°-150°F. resulted in a uniform, but less firm gel (H-5, H-6). Hydrochloric acid gels (without nitric acid) exhibited the same stratification (H-76, M-18). This was attributed in part to a wetting problem when the cellulose acetate powder was added to the liquid acid. Addition of a surfactant reduced the gas entrapment but caused a loss of firmness which made the gel unsatisfactory for subsequent etching. Addition of dibutyl phthalate increased viscosity of the liquid mixture, but a less firm gel resulted. The stratification, however, was overcome. The phenomenon was not detected in prior experiments since smaller gel specimens were prepared in shallow, non-transparent molds.

Syneresis, or the exuding of small amounts of liquid from the gel, is followed by shrinkage and warping. This was previously reported for Carbopol gels (C-24, C-26, C-30, C-32, C-35, C-45) and for various carboxymethylcellulose gels (L-3, L-5, L-7, L-9, L-14). However, in the cellulose acetate gels, syneresis was insignificant, presumably because of the smaller specimens.

During the reporting period just completed, the problems became more apparent as specimen size increased. For example, a gel of 432 grams cellulose acetate and 1,440 cc. acid solution aged in closed containers as follows (H-31):

Gel Acid Strength	Days Aged*	Liquid Exuded**	Shrinkage**
(a) Strong Acid $6\underline{N}\ H^+$, $2\underline{M}\ NO_3^-$			
	4 days	145 cc.	½" in 12"
	8 days	15 cc.	---
	12 days	---	---
(b) Weak Acid $3\underline{N}\ H^+$, $2\underline{M}\ NO_3^-$			
	4 days	280 cc.	7/8" in 12"
	8 days	140 cc.	---
	12 days	40 cc.	---

* Cumulative
** Incremental

The comparative effects of aging in open and closed containers were determined for 18-inch lengths of gel formulation (a) above(H-32). The uncovered gel warped and cracked in two days, and after six days had separated in several places. Total shrinkage was 1½" in 18". The covered gel did not warp or crack even after fourteen days, but total

shrinkage was 3/4" in 18".

Syneresis, occuring in fresh gels, is detrimental to the etching process. Cuts are uneven and surface finish is inferior. A number of different ways of eliminating or reducing this phenomenon were tried with little success. Heating the cellulose acetate and acid mixture to 110°-150°F. before gelation produced more uniform gels, but still with appreciable syneresis and a loss of firmness (H-5). Cooling to 60°F. had little effect other than to increase gelation time (H-26). Cooling to 38°F. reduced syneresis by only a small amount (H-12). The addition of small amounts of inhibitors such as ethylenediamine tetraacetic acid (H-25) or small amounts of salts (H-54) had no appreciable effect. The use of other acids, such as HF (M-36, M-39),, and the substitution of potassium dichromate for nitric acid (L-38) were similarly ineffective, and in some cases failed to gel.

Until syneresis can be prevented, gels must be aged in closed containers for best etch results. The syneresis decreases substantially after a few days aging and after four to ten days, depending on the acid strength, is essentially complete. It is further advantageous to wipe any remaining liquid acid from the gel surface prior to etching.

In formulating cellulose acetate gels, it was found that the variation in the chemical nature of the raw material demands a single source of supply in order to achieve consistent results at this stage of the laboratory work. In all but one experiment, Eastman E394-30 grade of cellulose acetate was used. To date, no significant differences have been noticed in different lots of this material. With a duPont product (H-9), there was a smaller range of formulation which would produce good gels. Generally, these gels were not as firm and syneresis was more pronounced. Presumably, there will be greater latitude of formulation with continued development of gel systems.

Although most work during this period was with the cellulose acetate (CA) gels, there was some work with carboxymethylcellulose (CMC) gels formulated with different liquid etchants. CMC gels were prepared with the following liquid systems: HCl (M-72, L-30); HF-HNO_3 (M-74); HNO_3-NH_4F-HF (L-29); $Fe(NH_4)_2(SO_4)_2$-H_2SO_4 (L-31); $NiSO_4$-$NiCl_2$-H_3BO_3(M-77); HF-$NiCl_2$-Na_2SO_4(M-90); HCl-HNO_3-H_3PO_4-$FeCl_3$(M-62). Varying degrees of syneresis were observed in all of the above gels.

It should be noted that both CA and CMC are able to gel a wide variety of liquid etchants of various acids and salts, individually or mixed. This permits many preliminary experiments to be conducted on liquid etchants prior to gelling them.

I - Discussion - continued

B. ELECTROLYTIC CHEMICAL ETCHING

It was recommended in the last Interim Report that methods of increasing the effectiveness of semi-solid etchants by supplementing chemical energy with electrical energy be investigated, and that methods be sought for eliminating gas evolution at the workpiece.

A considerable part of the activity during this period was devoted to the study of the effect of passing a direct current through the semi-solid etchants with the workpiece being the anode.

In previous work involving metal removal with chemical energy alone, the driving force was the decrease in free energy which takes place when free metal changes to the metallic ion. But the evolution of gas at the metal-gel interface increases the resistance to this process. Ionic diffusion through the semi-solid etchant is caused by an ion concentration gradient progressing through the gel mass. Application of an electromotive force across the anodic workpiece and the semi-solid etchant should increase the rate of metal removal by adding extra electrode potential (increasing the driving force) and by decreasing the resistance through elimination of gas evolution at the workpiece.

It was found that the use of direct current through the system increased the etch rate and reduced or eliminated the gassing (L-30, M-1, H-8, H-20). However, the effect of the direct current on the rate of diffusion of reaction products through the gel has not been conclusively determined. Positive determination depends on a more abstract study of mass diffusion through gels and the effects of various EMF applications.

Electrolytic etch studies were made on different gels, rigid porous solid systems, and on liquid etchant systems. The study of factors affecting the depth and surface finish of the etch included etchant composition, voltage and current density. Current densities and voltages used were in the order of 0.6 amp. per square inch and 3 volts. Current efficiency up to 75% was obtained (L-36).

Gel composition and thickness also received attention (M-3, M-6 through M-10). For example, Figure 2 shows the electrical resistance of the cell to be directly proportional to gel thickness. But it was separately determined (M-90, M-96) that an increase from ½" to 1" thickness of gel did not result in a commensurate increase of etch depth. An increased amount of CMC gelling agent resulted in lower etch rates (M-69). Similarly, it was found that a decrease in pore size of a rigid, porous carrier matrix resulted in lower etch rates (M-117).

It was found that soon after application of the voltage the current would decrease with an accompanying reduction in etch rate (L-31, M-12, M-90, M-102, and Figure 3). The current reduction was due in many

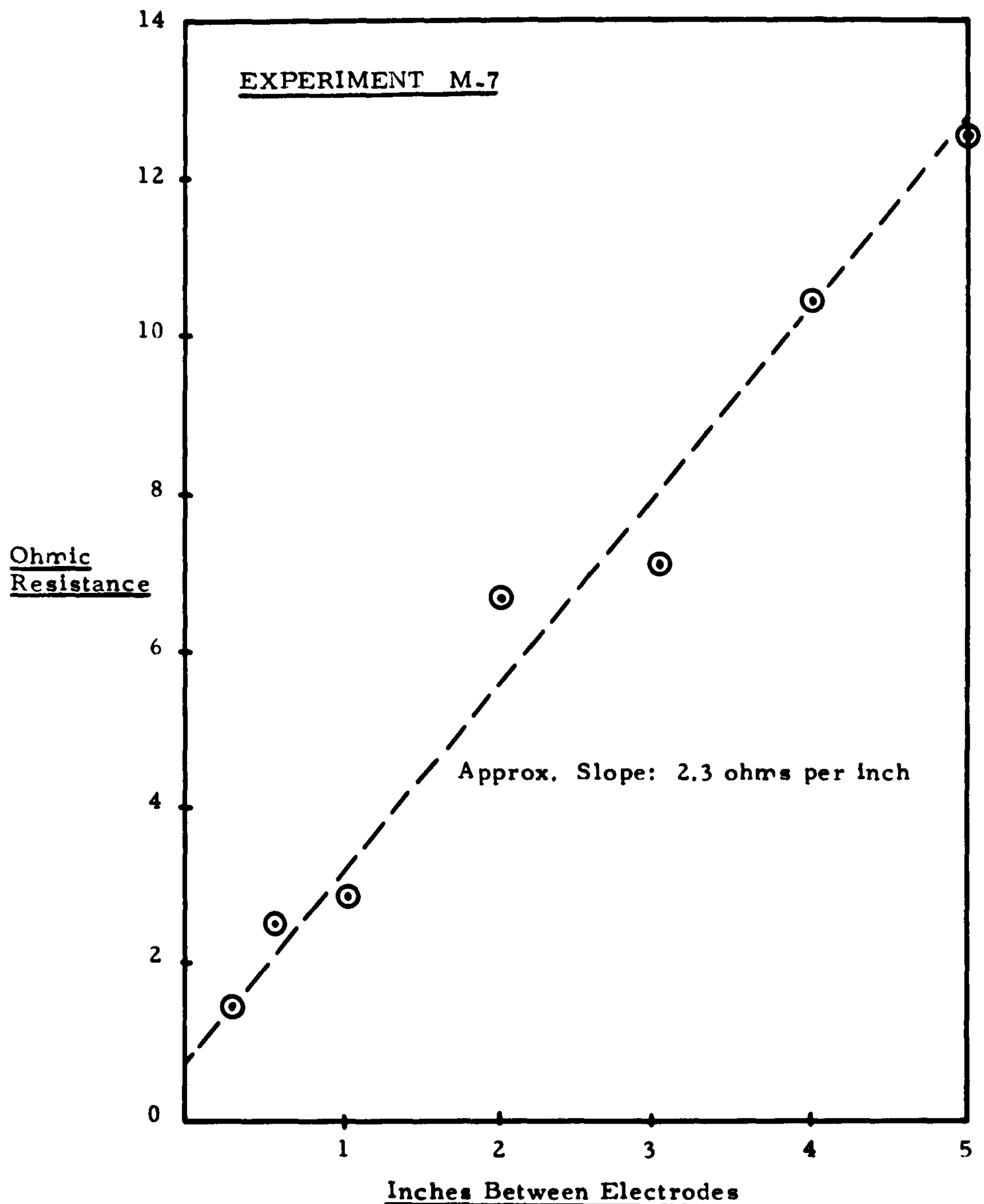
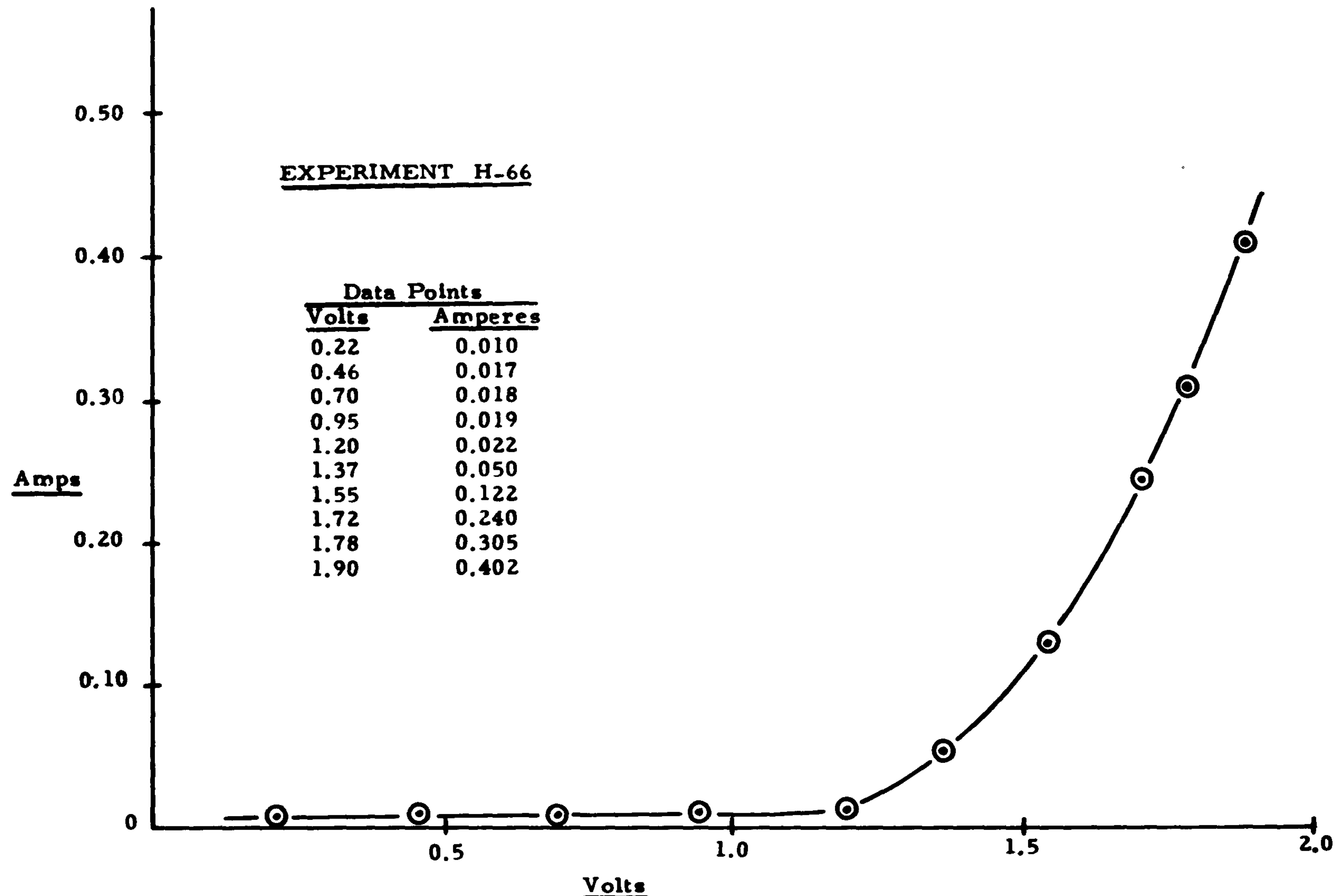


Figure 2 - Dependence of initial ohmic cell resistance on the thickness of gel separating the electrodes, at 5 volts potential.



Data Points

Volts	Amperes
0.22	0.010
0.46	0.017
0.70	0.018
0.95	0.019
1.20	0.022
1.37	0.050
1.55	0.122
1.72	0.240
1.78	0.305
1.90	0.402

Figure 3 - Typical change in initial cell current with an increase in potential for cellulose acetate gels.

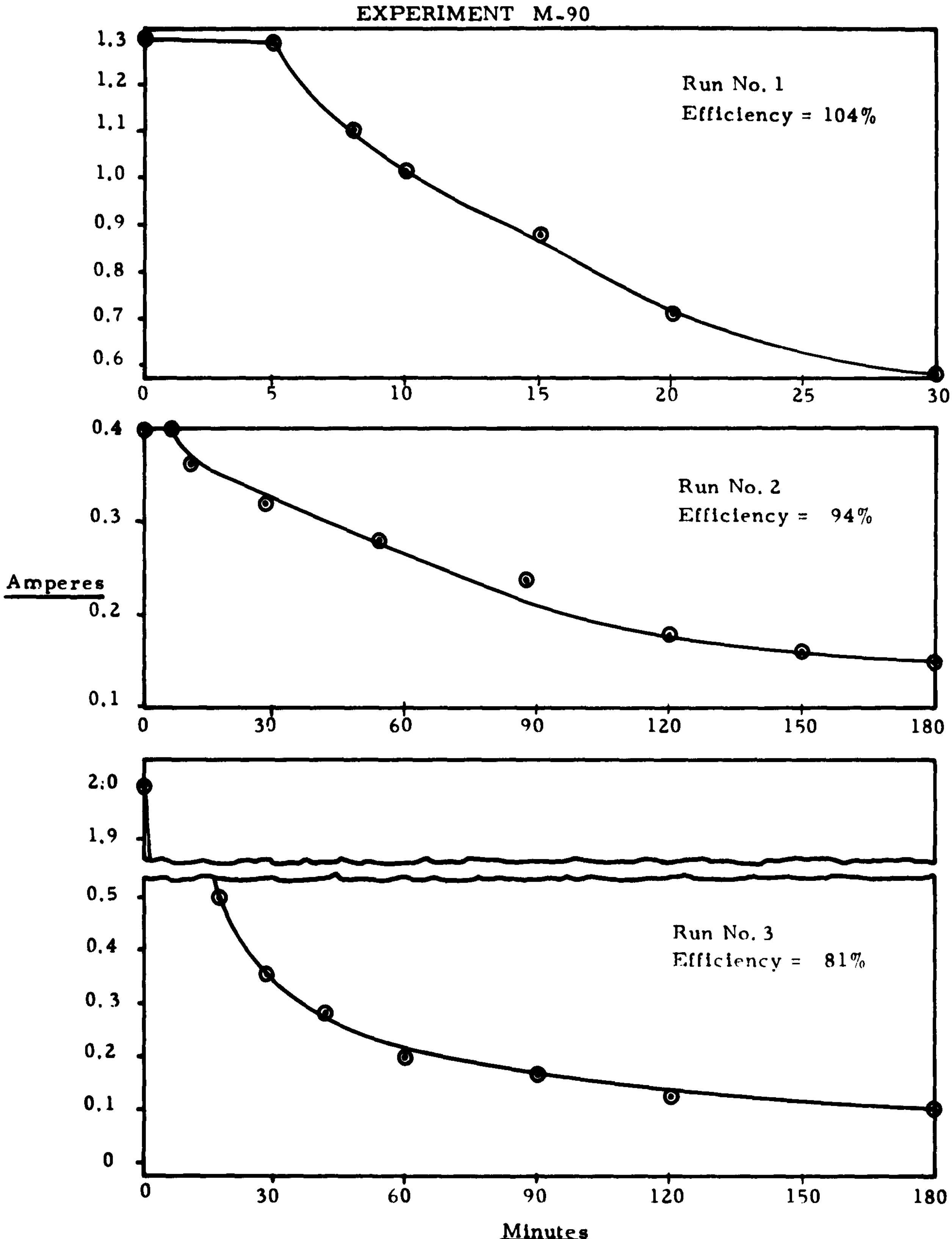


Figure 4 - Effect of initial current and potential on the development of cell polarization for carboxymethylcellulose gel.

cases to polarization caused by a black insoluble deposit formed on the anodic workpiece (Figure 4). Spectrographic analysis of the deposit revealed that the elemental complexes were heavily overlaid with titanium and were insoluble in the $HCl-HNO_3$ acid system. In some cases, where no film was formed, polarization was apparently due to increasing concentration of soluble salts near the anode (M-90). This emphasizes the importance of removing reaction products from the vicinity of the anode.

Attempts to prevent polarization and current drop included intermittent use of direct current, imposition of an alternating current on the direct current, ultrasonic vibration and low frequency vibration (M-13, M-72 through M-75, M-92, M-122 and Figure 5). All of these approaches were unsuccessful.

Removal of reaction products by replenishing the liquid etchant during the etching process was also investigated. In one technique, the cutting tool (i. e., the gel or the rigid porous solid) was partially submerged in a reservoir of liquid etchant. There was considerable improvement in removal of reaction products from a gel (L-33, L-37) and from rigid porous solids (M-102, M-104), but a steady-state process was not attained. There was still a gradual congestion of reaction products accompanied by polarization. In a second technique, liquid etchant was forced under a small positive head to flow through the cutting tool. The reaction products were removed at various predetermined rates, but control of line definition and surface smoothness was lost (H-80, M-125 through M-128).

Work is proceeding on a study of regenerative systems in which metal dissolves at the anode and deposits on the cathode with little or no change in the composition of the liquid etchant or electrolyte. Initial experiments were conducted with conventional plating solutions although it is recognized that plating primarily involves depositing metal at the cathode, while this effort is primarily concerned with removing metal from the anode. Some preliminary experiments (L-31, L-32, M-75, M-76, M-80) did not result in steady-state processes (i. e., were not regenerative), but work is continuing in this area.

C. ETCHING PLATE STOCK WITH ELECTROCHEMICAL GELS

The previously reported work on etching stainless steel plate stock (Types 302 and 321) with chemical gels resulted in low etch rates and comparatively poor surface finishes. These faults were due to the problems of gassing, build-up of solid reaction products at the gel-workpiece interface and limitations of the chemical energy which could be contained within the gel etchant. The use of elevated temperatures to increase etch rate and depth resulted in drying and degradation of the gels. The most successful technique was that of placing the metal

5(a) 1.3 volts DC
0.43 volts AC, 60 cps

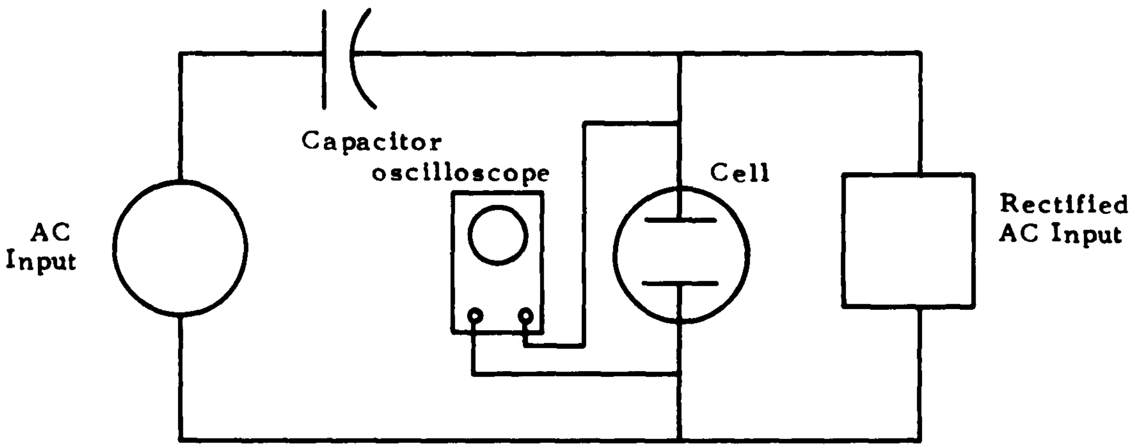
5(b) 1.3 volts DC
0.7 volts AC, 60 cps

5(c) 1.3 volts DC
1.0 volts AC, 60 cps

AC Input : 110 volt, 60 cycle variable transformer

Rectifier : 12 volt, 35 amp. selenium

Capacitor : 1,720 mfd



Circuit diagram for combined AC-DC experiment

Figure 5 - Typical wave forms produced by combining a rectified AC potential with an unrectified AC potential. The rectified wave form is shown with and without the added AC potential. Suitable combinations cause a reversal of the current 60 times each second.

plate on top of the gel which was partially immersed in a reservoir of liquid etchant. Under these conditions at 130°F. temperature, 4 to 6 mils of metal were removed in 120 minutes leaving a fairly smooth etched surface with reasonable line definition (L-26). Longer etch time resulted in only slight increases in metal removal.

During this work period, it was found that passing a small direct current (about 0.25 amp./square inch at 2.3 volts) through the gel increased the etch rate to 4-5 mils in 100 minutes (L-35), despite the fact that this experiment was made with acid etchant of half the strength of that in L-26, and at a temperature of 70°F. instead of 130°F.

Excessively high current density (in this case, greater than 0.40 amp./square inch) tended to make the gel crack and lose liquid(M-1, M-2, M-3, L-34, L-50, H-71). Lower current density (about 0.05 amp./square inch) merely prolonged the etch time and served no particular advantage (M-41).

Although polarization due to gassing at the workpiece was eliminated, as previously discussed in subsection B., the accumulation of either soluble or insoluble desposits at the anodic workpiece caused a decrease in current flow and etch rate (M-27, M-35, H-67). Acid concentration had no effect on polarization caused by these deposits (L-34, L-41).

The etching performance of gels containing only HCl compares with those containing HCl-HNO_3 mixtures as follows (L-34, L-42, L-45, M-11, M-15): Gels containing no nitrate ion appear to have greater resistance to deterioration and produce a good etch with extremely bright and smooth surfaces, but they develop a sludge at the gel-workpiece interface which acts as a barrier to diffusion of reaction products through the gel. The presence of the nitrate ion produces a dull surface on the etched metal, but apparently alters the anodic products to a more soluble and more diffusible state. Migration of reaction products through the gel proceeds at a very slow rate as indicated by a color change in the gel. A green coloration, due to chrome and nickel, occurs readily on the surface of the gel soon after contact with the metal workpiece. The progression of the color, indicating migration of reaction products, continues through the gel very slowly. Even after the chemical energy is expended in etching, the migration continues until the entire thickness of the gel is colored.

The most successful removal of reaction products was accomplished by replenishing the liquid etchant during the etching process. Partially submerging the gel in a reservoir of liquid etchant was previously noted. Small grooves, or drain channels, cut in the sides and face of of the gel contributed to the increased etch rate but resulted in uneven metal surfaces and some loss of line definition (L-50).

Another method investigated was to replace the gel after a period of time. By using the electrochemical etch combined with liquid acid replenishment and periodic changes of gel, deep cuts in plate stock (up to 70 mils deep) were achieved with fairly good line definition and surface finish (L-50, L-51, H-61, H-66, H-67, H-74, H-75). Figure 6 illustrates one cut of approximately 67 mils depth which was attained in 121 hours using six gel changes.

A limited amount of work was done with titanium alloys (L-29) and Inconel-X (H-51, M-90, M-97) but it is insufficient to evaluate at this time.

Figure 6. Deep cut in type-321 stainless steel plate. Sample was inverted over shaped gel surrounded by a reservoir of Liquid Electrolyte (Expt. L-37).

D. ETCHING HONEYCOMB CORE WITH ELECTROCHEMICAL GELS

During this reporting period, significant progress was made in shaping honeycomb core materials, particularly in the increased etch rate and in the definition and quality of cuts. As previously reported, the "press in" application was rejected in favor of the "walk in" technique using two stages of etching at ambient temperature. The first stage was a rough cut of about 1/2-inch depth attained in 24 hours, made with a gel of low shear strength. The second stage was a finishing cut of less than 1/16-inch in 24 hours, made with a gel of high shear strength. This technique was quite successful as demonstrated by the accurate reproduction of a 1½ inch diameter spheroidal surface to which the gel had been cast.

I - Discussion - continued

In the present period, there was significant progress, particularly in reducing the etch time from many hours to a matter of minutes by the application of a direct current to supplement the acidic gel. The process was also reduced to a single stage operation and control of shrinkage and warping was improved for larger gel specimens. Etching larger sizes of stainless steel honeycomb (17-7 PH and PH 15-7 Mo) demonstrated the feasibility of this process and revealed some problems which were not totally unexpected.

For making "walk in" cuts, it was necessary to devise apparatus to position the honeycomb over the gel and to control the rate of penetration. Figure 7 shows the experimental equipment used to make flat cuts (i. e., overall reduction of core thickness), single and double step cuts simulating edge member recesses, and wedge cuts (Figure 8 and 9). Cut sizes ranged from 4 square inches to 81 square inches.

Table I summarizes the more important aspects of this portion of the work. In general, the metal surface finishes were good. In those cases where the gel warped, the depth of etch was uneven but the surfaces of the individual cell walls were flat and good. A comparison of experiments listed in Table I shows that the application of direct current increases the etch rate by 10 to 25 times that attainable by straight chemical action (H-39 vs. H-46, H-48), and that the etch rate varies directly with the amount of current (H-40, H-42, H-46, H-48). This effect is much more pronounced with honeycomb than with solid plate stock because of the much greater ratio of interfacial surface area per unit weight of the metal. There is a proportionately greater cross-sectional area of gel in contact with the metal which enables reaction products to diffuse more readily.

Evaporation loss of acid volatiles warped the larger gel specimens and resulted in uneven depth of etch until the gel and honeycomb were completely submerged in a dielectric liquid (kerosene) during the electrochemical etching process (H-95). The liquid environment (1) prevents evaporation and consequent warping of the gel during the process, (2) prevents attack by acid vapor on the exposed walls of the honeycomb cells, (3) provides a heat exchange medium to control temperature, and (4) facilitates removal of reaction products which disperse more freely and ultimately settle to the bottom of the containing vessel. Figure 10 illustrates the experimental setup and Figure 11 shows the excellent finish obtained in an overall reduction of thickness of a 16 square inch core specimen.

One test conducted with AM 350 stainless steel honeycomb with 4 mil wall thickness indicates that changes may be required in current density and/or gel composition before a flat, uniform cut can be made in this alloy (H-90).

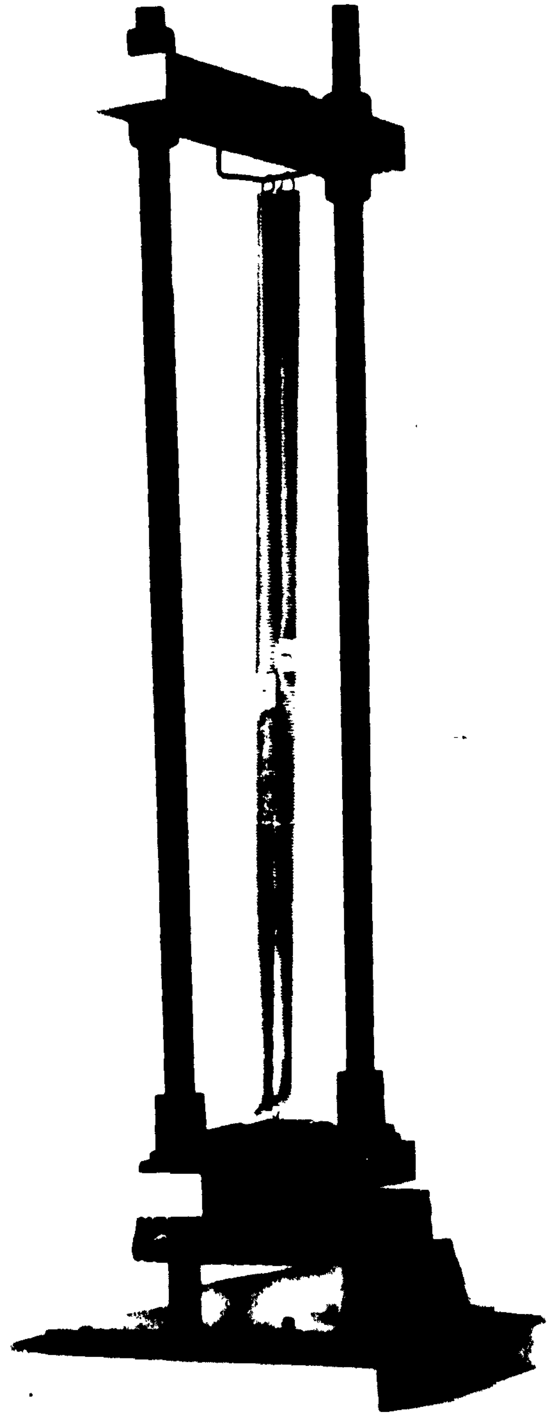


Figure 7 - Apparatus used to position honeycomb specimens for chemically milling with gels. The wedge-shaped gel on the platform was used to produce the tapered specimen shown in Figure 9.

Figure 8 - Diagonal step cut produced by chemical action of the gel (Expt. H-11). Compare the finish with that obtained when electrochemical milling is used (Figure 11).

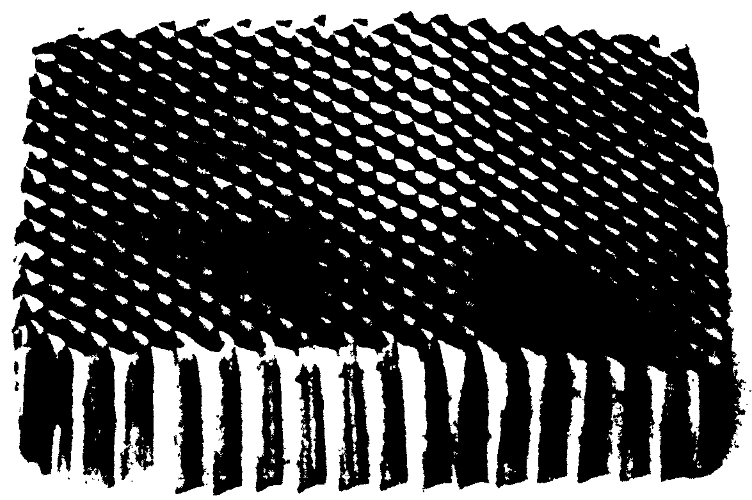


Figure 9 - Wedge cut on 17-7 PH stainless steel honeycomb core.

TABLE I

FLAT CUTS (OVERALL THICKNESS REDUCTION) IN 17-7 PH STAINLESS STEEL HONEYCOMB

Cell Wall Thickness: 1½ mils

Gel Etchant: Cellulose Acetate containing 36g. C. A., 120 cc. acid 3N H^+, 1M NO_3^-, aged 6 to 12 days.

Exp. No.	Cut Area (sq. in.)	Depth of Cut	Time Req'd	Amps-Volts	Remarks
L-24	Previously	reported as finishing operation Less than 2.6 mils/hour		0 - 0	To remove nodes from weld junctions.
H-39	4	30 - 33 mils	20 hours	0 - 0	Flat except where gas was trapped
H-40	4	25 mils ± 3	85 min.	0.6 @ 2.0	Slight nodes at welds
H-42	4	30 - 35 mils	120 min.	0.4 @ 2.7	Slight nodes at welds
H-46	4	15 mils	65 min.	0.3 @ 2.0	Flat
H-48	4	25 mils	35 min.	0.8 @ 3.0	Very flat
H-55	5	25 mils ± 1	35 min.	0.85 @ 2.6	Slight nodes
H-56	5	21 mils ± 2	30 min.	0.82 @ 2.7	Flat
H-57	5	20 mils ± 1	35 min.	0.74 @ 3.7	Flat
H-58	5	25 mils ± 1	35 min.	0.77 @ 2.8	Good
(1) H-91	16	50 - 100 mils	180 min.	1.6 @ 3.1	Gel warped, convex cut, 50 mils at flat center, 100 mil at perimeter
(1) H-92	16	50 - 70 mils	155 min.	2.0 @ 3.3	(As above)
(1)(2) H-93	16	40 - 55 mils	90 min.	2.0 @ 3.2	(As above)
(1)(2) H-94	81	10 - 30 mils	60 min.	5.7 @ 3.2	(As above)
(1)(2)(3) H-95	16	50 mils	120 min.	1.6 @ 3.0	No gel warping, surface good

Notes: (1) PH 15-7 Mo stainless steel core specimens.
(2) Gel placed on top of core. All others with core over gel.
(3) Submerged in kerosene during etch process.

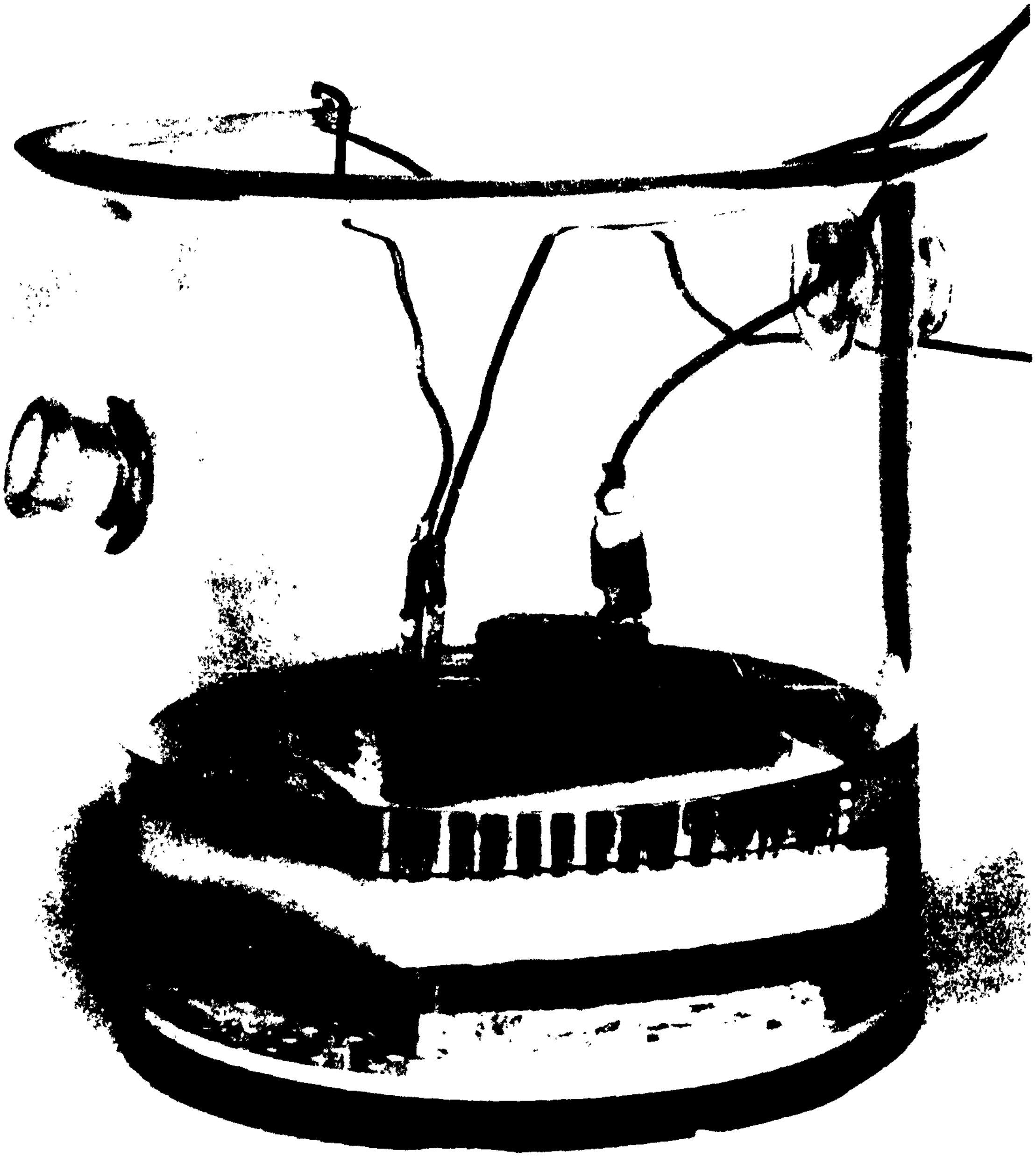


Figure 10 - Electrolytic cell with cellulose acetate gel electrolyte between honeycomb electrodes. Dielectric liquid environment prevents evaporation losses from the gel.

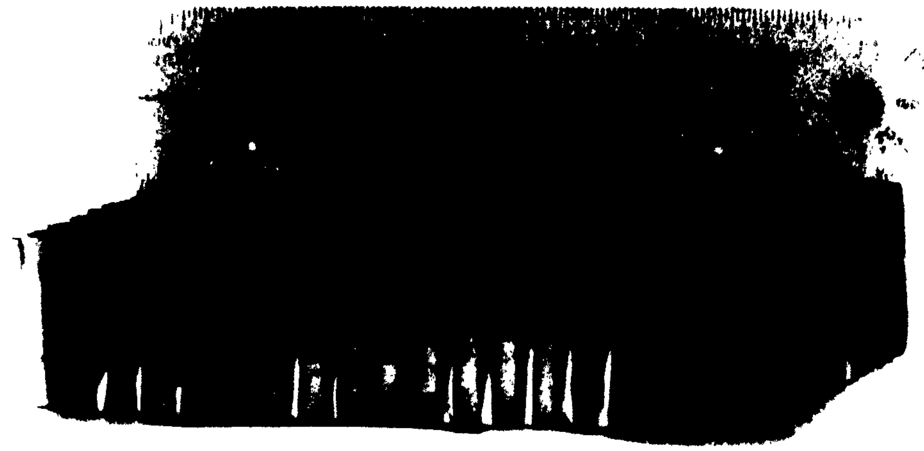


Figure 11 Smooth finish and uniform depth of cut produced on honeycomb with the apparatus shown in Figure 10. The thickness of the entire sample has been reduced by .050 inches (Expt. H-95).

E. RIGID, POROUS SOLID SYSTEMS

The previously reported work on configured solids of porous materials for liquid etchant delivery revealed some difficult problems. Dimensional control and surface finish of the etched specimens were unsatisfactory.

During the present period, an EMF was applied across the porous solid system with the metal workpiece as the anode. The general results obtained have been summarized in subsection B. of this report. An accumulation of reaction products between the metal and porous solid causes polarization which seriously retards the etching process. These reaction products tend to obstruct the porous solids as they do the gels. Similar attempts were made to remove them (e. g., mechanical vibration, small holes drilled in the porous solids and slight hydrostatic heads to induce flow), but these were not successful (M-118, M-119, M-121, M-125, M-126, M-127). It was found that an increase in pore size of the solid resulted in higher etch rates, but at the expense of dimensional control and surface finish, both of which were extremely poor (M-117).

The etching characteristics of the rigid porous solids were compared with those of a cellulose acetate gel using the same liquid etchant system. In all cases it was found that while the gel system does not remove metal as fast as the rigid porous solid system, the etched surfaces obtained with the gel systems are far superior in definition and finish (M-98, M-99, M-101, M-103, M-104, M-105).

F. LIQUID ETCHANT REACTIONS

Considerable work was done with liquid etchants in order to conduct a more abstract study of the reactions and to develop satisfactory etchants before attempting to form gel etchant systems.

Polarization occurred in many of the liquid etchant studies with imposed electrical currents. In cases where the reaction products were soluble, polarization was minimized by proper orientation of the anode so that reaction products were removed by natural convection through the etchant-electrolyte.

SECTION II
CONCLUSIONS

A. THE GEL SYSTEMS

Carboxymethylcellulose and cellulose acetate are the two most feasible gelling agents for acid etchants. Due to gradual hydrolysis, cellulose acetate requires greater gelation time, but it results in a firmer gel.

The temporary separation of gel and acid during the gelation process can be largely prevented by addition of surfactants and other agents, but with some sacrifice in gel consistency. The diffusion of reaction products through the gel is retarded in the region where liquid separation occurred in the gelation process. Further study is required to verify the apparent correlation and to eliminate the problem.

Syneresis is a problem inherent in freshly made acid gels. The result is a 10-15% loss of acid within a period of several days after gelation is complete. It is accompanied by severe shrinkage and warping. The process is essentially complete after an aging period of 4 to 10 days. Shrinkage and warping can be minimized by aging the gels in closed containers.

Liquid acid exuded during the etching process causes an uneven cut. Until syneresis can be controlled or eliminated, gel aging is required. Because of shrinkage, cuts are presently limited to flat or straight configurations. In order to make profiled step cuts, or to etch large contours or cavities, gel shrinkage must be consistently predictable. It must also be minimized so that shrinkage which occurs while etching is within dimensional tolerance.

B. ELECTROLYTIC CHEMICAL ETCHING

Applying a direct current to the chemical etching system increases the rate of etch and largely prevents the accumulation of gaseous reaction products.

Electrical resistance of the cell is directly proportional to the thickness of the gel etchant, but depth of etch is not.

Soon after the current is applied, cell resistance increases due to polarization and the etch rate is sharply decreased. Polarization usually occurs as a deposit of insoluble reaction products at the anodic workpiece. But in some cases, this is attributable to soluble salts which leave no visible film.

II - Conclusions - continued

Intermittent application of direct current, superimposed alternating current, and applied vibration through the ultrasonic frequency range are unable to prevent polarization.

Replenishing the gel etchant by positive flow or partial immersion in liquid etchant improves removal of reaction products, but a steady state process is not presently attainable.

There is promise in regenerative systems in which metal dissolves from the anodic workpiece and deposits on the cathode with little or no change in the composition of the liquid etchant electrolyte.

Removal of solid reaction products continues to be a problem. It will require further study of mass diffusion through gels and the effects of various EMF applications. Some benefit may be derived from the replenishment technique or the regenerative technique, but the results to date are inconclusive.

C. ETCHING PLATE STOCK WITH ELECTROCHEMICAL GELS

Passing a small direct current through the gel etchant improves the etch rate slightly. The greater advantage is the ability to etch at ambient temperature with less acid strength, and the elimination of gaseous reaction products. The result is a smoother finish with better line definition.

Insoluble deposits still accumulate at the anodic workpiece. Acid concentration has no effect on this type of polarization. Excessively high current density cracks the gel, causing a loss of liquid etchant. Low current density merely prolongs the etch time.

Gel etchants without nitrate ions have greater resistance to deterioration. In the electrochemical process they produce a bright and smooth surface on steel plate stock. But penetration is quite limited due to accumulation of solid reaction products at the interface. The presence of the nitrate ion produces a dull etched surface but alters the reaction products to a more soluble and diffusible state.

The application of electrochemical energy, if supplemented with etchant replenishment by the partial immersion of the gel, and periodic changes of gel to avoid accumulation of reaction products, will etch up to 70 mils depth with good line definition and surface finish. The initial gel applications produce a rough finish, but the final applications improve the surface to approximately 125 RMS. The rate of etch is still extremely low.

D. ETCHING HONEYCOMB CORE WITH ELECTROCHEMICAL GELS

Application of direct current to the gel increases the etch rate on steel honeycomb core by 10 to 25 times the rate of straight chemical action. This compares favorably with the rate of conventional liquid chemical milling for the same material. Further, the etch can be accomplished in a single stage rather than roughing and finishing with gels of low and high shear strength.

The etch rate on honeycomb varies directly with the amount of current applied. The greater effect on honeycomb is due to the higher ratio of interfacial surface area per unit weight of metal.

Uneven depth of etch, due to evaporation of acid volatiles and subsequent gel warpage, can be prevented by submerging the gel etchant and workpiece in a dielectric liquid. The liquid environment further prevents acid vapor attack on cell walls not imbedded in the gel, provides a heat exchange medium to prevent deterioration of the gel, and facilitates dispersal of reaction products.

The foregoing conclusions apply only to 17-7 PH and PH 15-7 Mo core materials. Test results for AM 350 are inconclusive.

E. RIGID, POROUS SOLID SYSTEMS

The conditions necessary to etch with the porous solid delivery systems at reasonable rates and without obstruction by reaction products also cause an unacceptable loss of dimensional control and surface quality.

Although metal removal is faster with the porous solid system, the definition and surface finish attainable with gel systems are far superior. The concept of liquid etchant delivery through a porous solid matrix-carrier is now considered infeasible.

SECTION III

RECOMMENDATIONS

Significant improvement in the quality and rate of honeycomb etching should be fully exploited by further development. Although the present system depends on a dielectric liquid environment, the possibility of developing other means of preventing gel shrinkage and warping should not be dismissed. Covering the gel with a thin protective coating of low shear strength may prevent syneresis as well as warpage. If successful, such protective coating would better serve the project objective of an essentially dry process requiring a minimum of apparatus or facilities. It is further advisable to conduct mechanical property tests on brazed panel specimens made with honeycomb cores cut by this method. It is now reasonable to believe that this laboratory process could be developed into a production method which would result in substantial cost savings for shaping steel honeycomb core. Therefore, it is strongly recommended that the project effort be continued and intensified on this portion of the work.

With respect to etching plate stock, the improvements noted in definition and surface finish are encouraging, but the rate of etch is still unsatisfactory. This is attributed to problems in removal of reaction products; problems which can be solved only by concentrating further study on mass diffusion through gels with and without supplemental energy. Such study is recommended at this time.

Due to the unsatisfactory results of liquid etchant delivery through rigid porous solids, the complexity of apparatus, and the lack of indications of improvement, it is recommended that pursuit of this concept be terminated.

The success of the electrochemical etching process and the advantages which accrue to both honeycomb and plate stock application warrant further development to prevent or reduce the polarization problem and particularly to determine optimum conditions of applied EMF and current density.

The most promising gel-acid formulations have now been determined on a largely qualitative basis. It is recommended that this portion of the effort be continued with emphasis on quantitative study to determine optimum formulations.

SECTION IV

PROGRAM FOR THE NEXT PERIOD

Additional work is planned on the gel systems primarily to determine optimum acid concentration for greatest etch rate with least syneresis.

The electrochemical etch process will be pursued further by determining optimum voltage and current density, by attempting to eliminate the polarization problem, and by continued development of the noted regenerative or de-plating technique for plate stock.

The study of mass diffusion through gels and the effects of supplemental energy in the diffusion process will be intensified in an effort to achieve reasonable rate and depth of etch on plate stock.

Specimens of steel honeycomb core will be cut to precise thickness by electrochemical etching. These will be used in brazed panels which will be subjected to preliminary testing of mechanical properties. A thin, low-shear gel coating, possibly parafin, will be developed and tested for ability to prevent syneresis, shrinking and warping. However, the work with dielectric liquids will continue.

Finally, the total project effort will be evaluated and presented in a final report, together with recommendations regarding future development and achieving the status of a production method.

APPENDIX A

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APPENDIX

BIBLIOGRAPHY

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APPENDIX D

TABULATION OF SPECIFIC EXPERIMENTS

Note: **Experiment numbers and page numbers are continued from previous interim report**

APPENDIX D

TABULATION OF SPECIFIC EXPERIMENTS

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-1	To investigate the effects of preparing a cellulose-acetate gel using an air blender instead of a Waring blender as was used in L-1721.	H-2005.1 18 g cellulose acetate (Type E-394-30) 60 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-.	The cellulose acetate was slowly added to the acid and mixed for 60 seconds at a medium rate and for 10 seconds at a rapid rate.	A separation midway in the gel occurred after 60 minutes. A large number of air bubbles were entrapped in the gel. The gel was quite firm after 12 hours and a thin slice of the gel showed a discontinuity of air bubbles at the observed separation. A higher bubble content was easily distinguished in the upper separation. A film of acid covered the gel.	Cellulose acetate systems gel more rapidly with less mixing; however, a separation occurs during gelling.	Further study planned.
		H-2005.2 54 g cellulose acetate (Type E-394-30) 180 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-.	The cellulose acetate was slowly added to the acid and mixed for 120 seconds at a slow rate. The mixture was placed in a 4000 ml beaker and cast in a wedge shape.	A separation occurred as in H-2005.1 and the mixture had gelled after 12 hours. This gel had only a small number of air bubbles entrapped which were not detrimental to the cast surface. The surface was covered with a thin acid film. After 1 week the gel shrank from a width of 5 inches to a width of 4-1/2 inches. The casting tended to leak acid.		
H-2	To examine the etching characteristics of the gel prepared in Expt. No. H-1.	H-2005.1	A 17-7 PH S.S. honeycomb sample was placed on the gel with a 64 g weight on the honeycomb. The "walk-in" technique was used and the whole system enclosed by a 4000 ml beaker.	After 24 hours a cut of 3/32 inch was made. The problem of nodes at the welded junctions prevailed.	The cut compared to the previous cuts using the cellulose-acetate gel.	Further study is planned with emphasis on eliminating the nodes at the junctions.

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-3	To observe the shrinkage of the cellulose-acetate gels when prepared and allowed to stand.	600 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3 120 g cellulose acetate (Type E-394-30)	Cellulose acetate added slowly to acid and mixed in the air blender for 2 minutes at a medium speed. The following were filled with the mixture and one of each type covered: 2 – 25 ml graduates 2 – large test tubes 2 – 100 ml beakers.	25 ml graduates. After 30 minutes a separation occurred in both graduates. The separation consisted of a top layer of cellulose-acetate mixture, a middle layer of acid, and a lower layer of cellulose-acetate mixture. Over a period of 5 days the upper and lower separations gelled leaving a middle separation of acid. These separations were equally spaced in the test tube. The shrinkage and leaking of the gel was not observable due to the separation at the end of 5 days. Uncovered graduate: original weight of gel – 25.85 g final weight of gel – 25.61 g Test tubes—separation occurred as in the graduates, however, after 24 hours the uncovered test tube had diffused together. The covered test tube did not diffuse together even after 5 days and therefore no shrinkage or leaking measurements were made. This diffusion of the cellulose acetate into the acid took place from both separations. After 5 days the uncovered test tube shrank 3/8 inch in 6 inches and 7 cc of acid leaked from the gel. Uncovered test tube: original weight of gel – 100.18 g final weight of gel – 97.8 g	Cellulose-acetate gels tend to gradually shrink after preparation and at the same time leak acid. This leakage of acid may be accelerated by the void left by the gel.	Further study needed to eliminate the separation and reduce acid leaking.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-3 (con.)				Covered test tube: original weight of gel – 104.0 g final weight of gel – 103.4 g 100 ml beakers—separation occurred as with graduates but the cellulose acetate had diffused together in 12 hours. After the 5-day period, the uncovered beaker shrank 3/16 inch in 2 inches with a corresponding leakage of 16 cc of acid. The covered beaker shrank 5/32 inch in 2 inches with an acid leakage of 27 cc. Much of the acid leaked in the uncovered beaker evaporated. Uncovered beaker: original weight of gel – 103.3 g final weight of gel – 90.85 g Covered beaker: original weight of gel – 102.7 g final weight of gel – 100.5 g		
H-4	To increase the viscosity of the cellulose-acetate gel and thereby prevent separation.	H-2014.1 24 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^- 2.4 g Polyox	The Polyox was added very slowly to the acid being stirred in a Waring blender at a low speed. The cellulose acetate was then added and the mixture was stirred for 60 seconds at high speed. The mixture was cast in a large test tube.	No separation occurred at any time, however, a large number of air bubbles were entrapped. The mixture gelled in 24 hours and shrank 1/16 inch in 1-1/8 inches in 36 hours. (Measured across diameter.)	This gel cannot be used without removing air bubbles.	No further investigation planned.
		H-2014.2 24 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^- 14.3 cc fluorocarbon latex (L-242)	The cellulose acetate was added to the acid and the fluorocarbon latex was added very slowly while at low speed. The mixture was then blended for 60 seconds at low speed and cast in a large test tube.	Lumps were incurred during mixing and a foamy cellulose acetate mixture formed on top of the liquid mixture. After 25 minutes an acid separation had formed between the foam and the mixture. This separation disappeared after gelling. The gel was very flaky and crumbled when cut. After 3 days a shrinkage of 1/16 inch in 1-1/8 inches occurred. A vertical stratification occuring after mixing disappeared upon gelling.	This gel cannot be used due to crumbly nature.	No further investigation planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-4 (con.)		H-2014.3 24 g cellulose acetate (Type E-394-30) 120 cc 6$\underline{N}$ H^+ and 2$\underline{M}$ NO_3^- 24 g Polyox 20 cc fluorocarbon latex (L-242)	Polyox slowly added to acid and blended for 20 seconds at high speed. The cellulose acetate was added and mixed for 20 seconds at high speed. The fluorocarbon latex was then added very slowly and the mixture blended for 30 seconds at high speed. The mixture was cast in a 400 ml beaker.	No separation occurred and the mixture gelled in 24 hours. A very thick layer of a viscous liquid (like maple syrup) surrounded the gel. This liquid layer was approximately 1/8-inch thick.	This gel would not hold a cast shape.	No further investigation
H-5	To determine the effects of heating a mixture of cellulose acetate and acid prior to gelling.	60 g cellulose acetate (Type E-394-30) 300 cc 6$\underline{N}$ H^+ and 2$\underline{M}$ NO_3^-	Add cellulose acetate to acid and mix in Waring blender for 90 seconds at low speed.		Very firm and very smooth gels were formed by heating. No air bubbles were present and there was no separation. Slight decrease in firmness noted.	Further investigation recommended.
			H-2017.1 Heat 75 ml of mixture to 110°F and observe.	Initially a 3/8-inch liquid film formed atop the mixture and then diffused into the mixture within 3 hours. In 24 hours the gel was very firm and had changed in color from a white to a light yellow. Slight shrinking and acid leaking was observed but there were no visible air bubbles.		
			H-2017.2 Heat 75 ml of mixture to 125°F and observe.	Generally the same results as H-2017.1 except for a decrease in viscosity after 4-1/2 hours. System gelled in 24 hours however.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-5 (con.)			H-2017.3 Heat 75 ml of mixture to 140° F and observe.	No liquid film occurred on mixture. Gelled quite a bit after 1 hour but decreased in viscosity after 3 hours and would not hold shape. Changed from white to yellow more rapidly than H-2018.1. After 24 hours gel was very firm and had experienced slight shrinking and acid leaking. Gel was a very good texture and had no air bubbles.		
			H-2017.3 Heat 75 ml of mixture to 150° F and observe.	Generally the same as H-2017.3 except for more rapid occurrence of phenomenon. Very good gel.		
H-6	To determine if separation occurs when a heated mixture is allowed to gel in a large test tube.	24 g cellulose acetate (Type E-394-30) 120 cc $6\underline{N}$ H^+ and $2\underline{M}$ NO_3^-	Add cellulose acetate to acid and mix in Waring blender at low speed for 2 minutes. Heat mixture to 150° F and cast in large test tube.	No separation of acid from the cellulose acetate occurred at any time. After 36 hours the mixture had gelled and had experienced syneresis.	The gel did not tend to separate, however the phenomenon of syneresis was still present.	For further milling of S.S. honeycomb samples where a smooth bubble-free gel surface is desired it is recommended that the method of heating the mixture of cellulose acetate and acid to 125° F-150° F be used.
H-7	To mill a 17-7PH S.S. sample of honeycomb core using a two-step technique.	Sample H-2017.3 (initial cut)	Step 1 Place honeycomb sample over the cast gel with 64 g weight atop the honeycomb. No initial embedding of sample.	After 16 hours a cut approximately 1/4-inch deep had been made. A scalloped cut, with high spots at the welded junctions, was made.		
		Sample H-2017.1 (finish cut)	Step 2 Place honeycomb sample over gel and apply potential across gel — making the honeycomb sample anodic. 64 g weight placed atop sample.	time = 0 i = 0.6 ampere V = 2.3 volts time = 10 min i = 0.6 ampere After this period the nodes had decreased leaving only a slight rolling effect on the surface. The sharp scallops had been almost completely removed.	Using a two-step technique such as this it is very possible that a flat finish may be obtained.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-8	To mill a 17-7PH honeycomb sample using the previous two-step technique with higher voltages and more time during the second step.	24 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^- (initial cut)	Cast mixture in 600 ml beaker after mixing for 2 minutes. Repeat Step 1 in Expt. H-7 using 128 g weight in place of 64 g weight.	After 12 hours a cut approximately 1/4-inch deep had been made. The scalloped finish was present.		
		36 g cellulose acetate (Type E-394-30) 120 cc 3 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^- (final cut)	Cast mixture in 100 ml beaker. Place honeycomb sample atop the gel with a 64 g weight atop the honeycomb. Apply a potential across the gel. After 10 minutes remove 64 g weight and continue for additional 10 minutes.	time = 0 i = 0.4 ampere V = 3.7 volts time = 10 minutes i = 0.4 ampere V = 3.7 volts 64 g weight removed time = 10^+ minutes i = 0.37 ampere V = 4.5 volts time = 20 minutes i = 0.37 ampere V = 4.5 volts After 20 minutes a cut of approximately 1/16 inch was made. A reversed scalloped effect was now present. The high spots were between the junctions.	The removal of the weight atop the honeycomb may be a factor reducing the nodes at the welded junctions.	Further study planned.
H-9	To investigate the gelling characteristics of cellulose acetate produced by Dupont.	H-2023.1 12 g cellulose acetate (Dupont) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Add cellulose acetate to acid and mix in Waring blender for 1 minute. Cast in 100 ml beaker.	Mixture very fluid after mixing. After 1 hour a 1-inch acid separation occurred at the top of the beaker. This sample did not gel even after 60 hours.	Cellulose acetate manufactured by Dupont is not as suitable for our uses as that produced by Eastman since the range of cellulose acetate that can be added is considerably smaller.	No further investigation planned.
		H-2023.2 18 g cellulose acetate (Dupont) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2023.1.	Mixture more viscous than H-2023.1 after mixing. After 1 hour, 1/8-inch acid separation occurred at the beaker bottom. This mixture gelled after 36 hours. Syneresis had occurred.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-9 (con.)		H-2023.3 24 g cellulose acetate (Dupont) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2023.1.	Mixture very viscous after mixing and could not pour from blender. After 1 hour, 1/8-inch acid separation at beaker bottom. Mixture gelled after 12 hours with considerable air entrapment.		
		H-2023.4 12 g cellulose acetate (Dupont) 120 cc 6 $\underline{N}$ HCl	Same as H-2023.1.	Very fluid after mixing. After 1 hour, 1-inch acid separation at top of beaker. The sample was mushy and did not gel firmly after 60 hours.		
		H-2023.5 18 g cellulose acetate (Dupont) 120 cc 6 $\underline{N}$ HCl	Same as H-2023.1.	Slightly greater viscosity than H-2023.4 after mixing. After 1 hour, 5/8-inch acid separation at top of beaker. After 60 hours mixture had formed unfirm gel. Syneresis present.		
		H-2023.6 24 g cellulose acetate (Dupont) 120 cc 6 $\underline{N}$ HCl	Same as H-2023.1.	More viscous than H-2023.4 after mixing but easily poured from blender. After 1 hour, 1/4-inch acid separation at top of beaker. Firm gel formed after 24 hours. Pronounced amount of syneresis.		
H-10	To investigate various gels for an electrolytic finishing step of 17-7PH S.S. honeycomb.	H-2027.1 36 g cellulose acetate (Type E-394-30) 180 cc 3 $\underline{N}$ HCl	Heat mixture to 130° F and cast in petri dish. Cut gel into 1-inch strips and place under honeycomb. Adjust voltage across gel to between 2 and 2.5 volts initially. Lower honeycomb sample 0.0127 inch after 5 minutes and again after 10 minutes. Remove from gel after 15 minutes.	time = 0, i = 1.0 ampere V = 2.5 volts time = 5 minutes i = 1.0 ampere, V = 2.5 volts lower 0.0127 inch i = 0.85 ampere, V = 2.5 volts time = 10 minutes i = 0.68 ampere, V = 3.5 volts lower 0.0127 inch i = 0.84 ampere, V = 3.0 volts time = 15 minutes i = 0.54 ampere, V = 4.2 volts Remove from gel. Scalloped effect is still present with nodes at the welded junctions.	The gels used may have an application for an initial cut but a higher cellulose acetate content is needed if a flat surface is to be obtained. Tempering of gels at a high temperature results in a mushy texture.	Further study recommended.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-10 (con.)		H-2027.2 36 g cellulose acetate (Type E-394-30) 180 cc 6$\underline{N}$ H^+ and 2$\underline{M}$ NO_3^-	Same as H-2027.1.	time = 0, i = 0.78 ampere V = 2.1 volts time = 5 minutes i = 0.71 ampere, V = 2.1 volts lower 0.0127 inch i = 0.72 ampere, V = 2.0 volts time = 10 minutes i = 0.72 ampere, V = 2.0 volts lower 0.0127 inch i = 0.72 ampere, V = 2.0 volts time = 15 minutes i = 0.71 ampere, V = 1.9 volts The finish again was scalloped with nodes at the welded junctions. These nodes were more prominent than those of Expt. H-2027.1.		
		H-2027.3 24 g cellulose acetate (Type E-394-30) 120 cc 6$\underline{N}$ H^+ and 2$\underline{M}$ NO_3^-	Heat mixture to 135° F and temper at 135° F for 45 minutes. Follow same procedure as H-2027.1 for finishing.	Mixture did not gel firm and was slightly mushy when cut. time = 0, i = 0.7 ampere V = 2.0 volts time = 5 minutes i = 0.7 ampere, V = 2.0 volts lower 0.0127 inch i = 0.72 ampere, V = 1.9 volts time = 10 minutes i = 0.72 ampere, V = 1.9 volts lower 0.0127 inch i = 0.72 ampere, V = 1.8 volts time = 15 minutes i = 0.70 ampere, V = 2.0 volts The finish was similar to H-2027.2 but the gel was not firm enough and the honeycomb embedded in the gel.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-11	To etch two samples of 17-7PH S.S. honeycomb core.	H-2036.1 168 g cellulose acetate (Type E-394-30) 840 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Blend mixture in Waring blender for 2 minutes at low speed and cast in step shape. Place one honeycomb sample with its sides parallel to the step and another sample at a diagonal to the step. Place a 64 g weight atop each gel.	After 36 hours a cut approximately 3/8-inch deep was made. The finish was scalloped with nodes at the welded junctions.	A very flat cut can be made using this two-step technique. The firmness of the final gel may be an important factor in producing the flat finish.	Further investigation planned.
		H-2036.2 252 g cellulose acetate (Type E-394-30) 840 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Blend mixture in air blender at a medium speed for 2 minutes and cast in step shape. Orientate the honeycomb samples from H-2036.1 and place 64 g weight atop each.	This gel was left in the mold for 3 days and had cracked due to shrinkage during that period. The gel was very firm (almost hard). After 4 hours the sample with its sides parallel to the step was removed. The surface finish was very flat. The previous scalloped surface had been completely removed. The diagonal sample was removed after an additional 12 hours. The finish was slightly scalloped due to embedding of the honeycomb in the gel by the weight.		
H-12	To determine the effect of a cold atmosphere on the syneresis of the cellulose acetate gels.	H-2031.1a 24 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Mix constituents for 2 minutes in a Waring blender at low speed. Allow to gel in refrigerator at 38°F.	Initially an acid separation in the middle of mixture. After 3 days the mixture did not gel firmly, however, no noticeable shrinkage occurred.	A cool atmosphere has a definite effect on the reduction of the syneresis.	Further study needed.
		H-2031.1b 36 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2031.1a	Slight acid separation at bottom which disappeared after 2 hours. After 16 hours, mixture had gelled but was not firm. Slight shrinkage (volcano type) occurred after 3 days.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-12 (con.)		H-2031.2a 24 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Mix for 2 minutes at low speed in Waring blender and place in refrigerator at 38° F for 1 hour. Remove from refrigerator and allow to return to ambient temperature.	An initial acid separation in the middle of the mixture. After 16 hours the mixture had gelled. Syneresis occurred after 48 hours and continued to 72 hours.		
		H-2031.2b 36 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Same as H-2031.2a	A slight acid separation occurred at bottom and disappeared after 2 hours. After 3 days gel had become very firm and syneresis had taken place.		
		H-2031.3a Same as H-2031.1a	Mix at low speed in Waring blender for 2 minutes and heat to 130° F. Place in refrigerator at 38° F.	After a period of 3 days gel became firm and was of a rubbery texture. No syneresis or noticeable shrinkage occurred.		
		H-2031.3b Same as H-2031.1b	Same as H-2031.3a	Mixture gelled quite firmly after 2 hours but did not become firm enough to use until after 16 hours. No acid leakage, however gel did shrink (volcano type) slightly in 3 days.		
		H-2031.4a Same as H-2031.1a	Mix for 2 minutes in Waring blender at low speed. Heat to 130° F and place in refrigerator at 38° F for 1 hour. Remove from refrigerator and allow to return to ambient temperature.	Mixture gelled very firm after 16 hours at which time syneresis was already present. After 3 days the effect of syneresis was comparable to gelation at ambient conditions.		
		H-2031.4b Same as H-2031.1b	Same as H-2031.4a	Mixture gelled very firm after 16 hours. Syneresis did not take place until after 48 hours. After a total period of 3 days the syneresis compared to gelation at ambient conditions.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-13	To observe a large gel prepared and allowed to gel in a refrigerator at 38° F.	288 g cellulose acetate (Type E-394-30) 960 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Mix for 2 minutes in air blender and allow to gel in refrigerator at 38° F.	After 2 days the mixture had gelled but was not firm and was very tacky. The gel could not be removed from the mold without damage. No syneresis was noted.	Gelation in cool atmospheres reduces syneresis and increases gelling time. The results indicate that the problem of gel shrinkage and acid leaking may be reduced or eliminated by gelation at temperatures below ambient (70° F).	Continued investigation needed in a temperature range above 40° F but below 70° F.
H-14	To prepare a large cellulose-acetate gel using more acid per cellulose acetate than previously.	126 g cellulose acetate (Type E-394-30) 840 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Blend for 2 minutes at medium speed in air blender and cast in step shape.	After 12 hours the mixture had gelled but a large split in the gel was present at the etching surface.	This split was presumably due to shrinkage of the gel during gelation.	Initial-cut gels should be limited to higher cellulose-acetate acid ratios for the present until the shrinking problem can be alleviated.
H-15	Make wedge cut in 17-7PH S.S. honeycomb core.	Initial cut: 108 g cellulose acetate (Type E-394-30) 360 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Blend in air blender for 2 minutes at medium speed and cast as wedge shape. Place honeycomb core over wedge with 64 g weight atop.	After 14 hours a 1/4-inch cut had been made at the deepest end. The finish was scalloped.	The long time taken to make desired cut was due solely to poor orientation. The pinholes may easily be eliminated by having the honeycomb inclined instead of the gel.	Further investigation planned.
		Finish cut: Same as initial cut.	Same as initial cut.	After 4 hours the scalloped finish was not completely flattened. The poor finish was due to poor initial honeycomb to gel orientation.		
		Second finish cut: Same as initial cut.	Same as initial cut.	After 2 hours the finish is not as flat as desired. Again the problem was poor gel to honeycomb orientation.		
		Third finish cut: Same as initial cut.	Same as initial cut except that this gel was allowed to set for two additional days prior to use.	After 2 hours the finish was flat. Small pinholes were present near the edges of the metal which were caused by acid collection.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-16	Etch 17-7PH honeycomb samples in the more complicated double step shape.	Initial cut: 192 g cellulose acetate (Type E-394-30) 960 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Mix in air blender at medium speed for two minutes and cast in double step shape. Place honeycomb samples over gel with 64 g weight atop.	After 36 hours both samples were the same and had been cut 3/8 inch. The surface was scalloped with high spots at welded junctions.	Using the two-step method of honeycomb cutting, the second (finishing) cut must be made over a short time to prevent additional scalloping.	Further study planned.
		Final cut: 288 g cellulose acetate (Type E-394-30) 960 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Mix in air blender at a medium speed for 2 minutes and cast in double step shape.			
			Sample "A": Place honeycomb over gel with 60 g weight atop and leave for considerable period of time.	After 36 hours "A" was fairly smooth on lowest step while being scalloped on second step (by step, I mean shape, not procedure).		
			Sample "B": Place honeycomb over gel with 60 g weight atop and place in refrigerator at 38° F for long period of time.	After 36 hours "B" was smooth (not extremely flat) on the lowest step while the second step was severely scalloped with the welded junctions being the low spots.		
H-17	To prepare a cellulose acetate gel with a weaker acid for finishing.	288 g cellulose acetate (Type E-394-30) 960 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Blend for 2 minutes in air blender and cast into step shape.	The mixture had not gelled firmly after 12 hours. After 24 hours gel is shrinking but still is not firm. After 36 hours the gel began to crack along the surface but was too tacky to be removed from the mold without damage. Gel was not usable.	The weaker the acid, the longer the gelation time for equal acid-cellulose-acetate ratios.	Investigate higher acid-cellulose-acetate ratios.
H-18	To investigate the properties of high cellulose acetate to acid-ratio gels using 3 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-.	H-2052.1 120 g cellulose acetate (Type E-394-30) 240 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Blend for 2 minutes in air blender and cast in petri dish.	This could not be cast due to the extreme viscosity of the mixture. This formulation was a paste with lumps of cellulose acetate throughout.	The 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^- cellulose-acetate gels do not seem appropriate at this time due to shrinkage, warping, and slow gelation. Here again, the results may be very dependent on the temperature.	Further investigation planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-18 (con.)		H-2052.2 1200 g cellulose acetate (Type E-394-30) 340 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Same as H-2052.1.	This mixture was pourable and gelled within 12 hours but was tacky. The gel could not be removed without damage due to tacky condition and therefore was not used.		
		H-2052.3 144 g cellulose acetate (Type E-394-30) 360 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Same as H-2052.1.	This mixture was also pourable and gelled within 12 hours but was tacky as H-2052.2. Gel could be easily removed after 16 hours, but after 36 hours had warped completely out of shape.		
H-19	To prepare a thick cellulose-acetate gel using 3 $\underline{N}$ H^+ ion and 1 $\underline{M}$ NO_3^- ion acid.	336 g cellulose acetate (Type E-394-30) 960 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Mix for 2 minutes in air blender at medium speed and cast into pyrex tray.	This mixture required 2 days to gel firm and lose its tackiness. A large number of surface cracks were present and the shrinkage was 1/2 inch in 10 inches. After 4 days gel had warped out of shape.	Thick gels of this type do not eliminate warping. These gels do not seem usable in this manner.	No further investigation.
H-20	To cut a 17-7PH S.S. honeycomb core using an initial electrolytic application.	36 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Mix for 2 minutes in air blender at medium speed and cast as flat strip. Place honeycomb sample over gel with 64 g weight atop and apply potential across the gel making honeycomb anodic.	time = 0, i = 0.8 ampere V = 2.0 volts time = 1 hour i = 0.67 ampere, V = 2.1 volts Diffusion of approximately 1/4 inch. time = 2 hours i = 0.67 ampere, V = 2.1 volts Had diffused completely through gel which was 3/8-inch thick. time = 3 hours i = 0.65 ampere, V = 2.25 volts Honeycomb sample removed from gel. Gel had cracked slightly during cutting. The depth of cut was 3/16 inch with the finish reversed scallop (welded junctions were low spots).	The time to produce a cut of any depth could be reduced considerably using electrical means. A finishing operation is still necessary.	Further investigation planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-21	To electrolytically etch a 17-7PH S.S. honeycomb sample over a long period to see if polarization takes place.	36 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Mix for 2 minutes with air blender at medium speed and cast as flat strip. Place honeycomb sample over gel with 64 g weight atop and apply potential across gel making honeycomb anodic.	time = 0, i = 0.9 ampere V = 1.0 volt time = 3 minutes i = 0.65 ampere, V = 2.0 volts Rapid voltage rise at this time. Current fluctuated ± 0.02 ampere time = 1 hour i = 0.65 ampere, V = 2.0 volts Current constant. Diffused 1/8 inch. time = 2 hours i = 0.66 ampere, V = 2.0 volts Gel seems to be breaking down. time = 3 hours i = 0.66 ampere, V = 2.2 volts Gel now was liquefying. time = 4 hours i = 0.61 ampere, V = 2.5 volts Gel still liquefying. Experiment stopped due to closeness of honeycomb to cathode. Honeycomb was cut 3/16 inch and the finish was reverse scalloped.	There is no polarization before the gel decomposes. The polarization expected seems to occur shortly after the voltage is applied and is overcome by the high current density at the contact points of the honeycomb.	Further study needed.
H-22	To cut a 17-7PH S.S. honeycomb sample using an initial electrolytic cut and a final "walk in" finish.	108 g cellulose acetate (Type E-394-30) 360 cc 6 N H^+ and 2 M NO_3^-	Initial cut: Mix with air blender for 2 minutes and cast in petri dish. Place honeycomb over gel with 128 g weight atop. Apply a potential across gel making honeycomb anodic. Gel thickness was 5/8 inch.	time = 0, i = 0.66 ampere V = 1.5 volts Current and voltage fluctuating. time = 2 minutes i = 0.49 ampere, V = 2.7 volts i and v constant. time = 20 minutes i = 0.57 ampere, V = 1.8 volts time = 1 hour i = 0.57 ampere, V = 1.7 volts Diffusion 1/8 inch. time = 2 hours i = 0.56 ampere, V = 1.8 volts time = 2 hours, 30 minutes i = 0.47 ampere, V = 2.75 volts time = 3 hours i = 0.47 ampere, V = 2.7 volts Honeycomb removed. A cut of 1/8 inch was made. The finish was scalloped with the nodes at the welded junctions (this is the reverse from the previous electrolytic experiments).	The cutting time for the initial cut was reduced greatly to 3 hours. The finish cut took a total of 26 hours with the actual finishing taking place only for the last 1-1/2 hours. This indicated that a comparable cut may be able to be made in 7 or 8 hours (or even more rapidly).	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-22 (con.)		Finishing cut: 336 g cellulose acetate (Type E-394-30) 960 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Mix in air blender for 2 minutes at medium speed and cast in pyrex tray. Place honeycomb sample over gel with 73 g weight atop.	Allowed to finish for 24 hours with no appreciable finishing noted (only finishing was slight reduction of scalloping). The weight was increased to 270 g and allowed to finish for 1 hour and 30 minutes. Very flat finish resulted with very slight blemishes at welded junctions.		
H-23	To investigate the effect of varying the area of honeycomb for the initial cut.	192 g cellulose acetate (Type E-394-30) 960 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	H-2060a Mix for 2 minutes in air blender and cast in pyrex tray. After gelation place honeycomb over gel with 100 g weight atop and apply a potential across the gel making honeycomb anodic. Honeycomb area = 8 square inches.	time = 0, i = 3 amperes V = 3.1 volts time = 5 minutes i = 3.3 amperes, V = 2.75 volts time = 10 minutes i = 3.41 amperes, V = 2.7 volts time = 20 minutes i = 3.41 amperes, V = 2.6 volts time = 40 minutes i = 3.42 amperes, V = 2.6 volts Depth of cut was approximately equal to 1/32 inch. Finish was slightly scalloped. Gel liquefication at surface.	Decreasing the area of the gel does not change resistance appreciably. The increase in cutting speed is probably due to increased current density at honeycomb contact edge and higher temperature of gel surface.	Further study planned.
			H-2060b Same as H-2060a except area of honeycomb is 4 square inches.	time = 0, i = 3.2 amperes V = 2.9 volts time = 10 minutes i = 3.2 amperes, V = 2.9 volts time = 20 minutes i = 3.2 amperes, V = 2.9 volts time = 30 minutes i = 3.25 amperes, V = 2.8 volts Cut depth approximately 1/8 inch. Finish is very severely scalloped. Gel liquefying at surface.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-24	To electrolytically etch honeycomb in the same manner as H-23 but in addition use stops to restrict depth of cut in an effort to reduce severe scalloping.	192 g cellulose acetate (Type E-394-30) 960 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2060a except stops placed to make 1/4-inch cut.	time = 0, i = 3.3 amperes V = 2.7 volts time = 30 minutes i = 3.3 amperes, V = 2.7 volts Honeycomb core is now resting on stops. time = 40 minutes Current is decreasing with increasing voltage. time = 60 minutes i = 0.3 ampere, V = 12.0 volts Current and voltage decreased steadily. Cut depth is 1/4 inch with a severely scalloped finish. Large area of honeycomb etched deeply probably due to restricted heat transfer due to weight atop.	This experiment is not conclusive that stops will not reduce severely scalloped finish.	Further investigation planned.
H-25	To investigate ethylenediaminetetraacetic acid (EDTA) as a syneresis retarding additive.	H-2055.1 1 g EDTA 24 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Blend in air blender for 2 minutes at medium speed and cast in 100 ml beakers.	After 24 hours syneresis took place. Syneresis appears to be similar to gels without EDTA.	EDTA has no syneresis inhibiting characteristics on cellulose acetate gels.	No further investigation planned.
		H-2055.2 2 g EDTA 24 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2055.1.	Same as H-2055.1.		
		H-2055.3 3 g EDTA 24 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2055.1.	Same as H-2055.1.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-25 (con.)		H-2055.4 4 g EDTA 24 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2055.1.	Same as H-2055.1.		
		H-2055.5 5 g EDTA 24 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2055.1.	Same as H-2055.1.		
H-26	To investigate the effect of cool of cool temperature conditions on cellulose acetate gels, noting especially syneresis.	H-2057.1 18 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Mix for 2 minutes in air blender at medium speed and cast in 100 ml beaker. Place in 60° F (approximately) atmosphere.	The sequence of gelation and syneresis was impeded by the 60° F temperature. The gelation time was increased and syneresis was delayed slightly.	The cool atmosphere had no effect other than retarding the normal reactions in cellulose acetate gels.	No further study at this time.
		H-2057.2 24 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2057.1.	Same as H-2057.1.		
		H-2057.3 36 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Same as H-2057.1.	Same as H-2057.1.		
		H-2057.4 18 g cellulose acetate (Type E-394-30) 120 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Same as H-2057.1.	Same as H-2057.1.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-26 (con.)		H-2057.5 24 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-	Same as H-2057.1.	Same as H-2057.1.		
		H-2057.6 36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-	Same as H-2057.1.	Same as H-2057.1.		
H-27	To ascertain the most favorable weight for "walk in" to honeycomb area for the best finish when using 6 N H^+ ion and 2 M NO_3^- ion acid.	H-2064.1 36 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Mix for 2 minutes with air blender and cast as flat section. Place honeycomb sample on gel with 50 g weight on honeycomb. Overall honeycomb area over gel of 4 square inches.	After 2-1/2 hours approximately 10 mils had been removed. Surface slightly rough.	60 g and 70 g samples gave best surface finishes for 4 square inches of honeycomb area.	Further study planned.
		H-2064.2 Same as H-2064.1.	Sa· · as H-2064.1 except 60 g weight used for 4 square inches honeycomb area.	After 2-1/2 hours approximately 10 mils removed. Surface flatter than 50 g sample.		
		H-2064.3 Same as H-2064.1.	Same as H-2064.1 except 70 g weight used for 4 square inches honeycomb area.	Cut and finish very similar to H-2064.2.		
		H-2064.4 Same as H-2064.1.	Same as H-2064.1 except 80 g weight used for 4 square inches honeycomb area.	Approximately 10 mils removed after 2-1/2 hours. Surface finish rough.		
H-28	Same as Expt. H-27 but using 3 N H^+ ion and 1 M NO_3^- ion acid.	H-2069.1 36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-	Same as H-2064.1 except 70 g weight used for 4 square inches honeycomb area.	After 10 hours surface flat with approximately 20 mils removed. Indentations at welded junctions.	The overall results seem to be very uniform indicating that they can be reproduced easily. Indentations in H-2069.1 do not seem to be detrimental to fabrication.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-28 (con.)		H-2069.2 Same as H-2069.1.	Same as H-2064.1 except 80 g weight used for 4 square inches honeycomb area.	Same as H-2069.1 with deeper indentations at welded junctions.		
		H-2069.3 Same as H-2069.1.	Same as H-2064.1 except 90 g weight used for 4 square inches honeycomb area.	Same as H-2069.1. Indentations at welded junction slightly deeper than H-2069.2.		
		H-2069.4 Same as H-2069.1.	Same as H-2064.1 except 100 g weight used for 4 square inches honeycomb area.	Same as H-2069.1. Indentations at welded junctions slightly deeper than H-2069.2.		
H-29	To make a controlled cut in 17-7PH honeycomb of 0.020 + .003 inches.	H-2066.1a 36 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Mix for 2 minutes with air blender and cast as flat section. Reference honeycomb so that depth of cut can be observed. 60 g weight atop.	After 4 hours 17 mils (approximately) were removed. Nodes were at welded junctions. Additional etch for 1 hour on new gel of same consistency resulted in etch of 20-24 mils with nodes lessened.	Results are not as consistent as desired. Rougher cut when bearing more uniform does not seem to follow.	Further investigation planned with weaker acid.
		H-2066.1b Same as H-2066.1a.	Same as H-2066.1a except 40 g weight placed on 20 g flat plate to give more even bearing on gel.	After 4 hours 15-16 mils removed. Nodes present. Additional hour on new gel of same consistency 19-25 mils with nodes judged too great for application.		
		H-2066.2a Same as H-2066.1a	Same as H-2066.1a except 70 g weight atop.	After 4 hours 19 mils removed. Additional hour 27-29 mils removed with slight nodes left at welded junctions.		
		H-2066.2b	Same as H-2066.2a except that 20 g plate with 50 g weight used to give more even bearing.	After 4 hours 18 mils removed with nodes at junctions. Additional hour on new gel 25-30 mils removed with surface nodes too great for application.		

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-30	To cut a 17-7PH honeycomb core using a gel that has essentially stopped extruding acid.	36 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Mix in air blender for 2 minutes at medium speed and cast into flat strip. Gel was removed from mold after 24 hours and then allowed to dry in air for an additional 5 days. Gel surface was dry (no acid film). Two honeycomb cores were placed over the gel with 15 g per 1 square inch honeycomb area.	After an etching time of 6 hours 10 mils were removed and both cores were very similar. The surface finish was very flat. No scalloping or indenting was present. There was no visible "knife edging" of the honeycomb. The gel surface was still dry with an absence of foam.	A very flat finish is obtained from gels which have stopped acid extrusion. No acid or liquid film is produced on the gel surface as a result of the etching reactions. This type of cutting operation is very promising if gel warping can be eliminated.	Further study planned.
H-31	To observe gels made with cellulose acetate and then allowed to stand over a relatively long period of time.	H-2071.1 432 g cellulose acetate (Type E-394-30) 1440 cc 6 N H^+ and 2 M NO_3^-	Mix for 2 minutes in air blender and cast as flat section in tray. Always keep gel in covered container.	After 4 days gel was removed from tray. 145 cc of acid had been extruded and a shrinkage of 1/2 inch in 12 inches had occurred. After 8 days the gel had extruded an additional 15 cc of acid but no further shrinkage had occurred. No warping or surface shrinkage had occurred. No warping or surface cracking yet. After 12 days no further acid extrusion or gel shrinkage. No surface cracks or warping but gel now is not as firm as 4- or 8-day period. Gel is unfirm only to extent that it is much easier to cut but in no way has it lost its original shape. A total of 160 cc of acid extruded in 12 days. Only 10 g were unaccounted for, presumably lost to evaporation.	Cellulose-acetate gels seem to shrink during the initial large amount of syneresis and then retain their shape quite well. The absence of warping and cracking observed in previous experiments is due to even drying (although very small) in closed containers. The 6 normal acid gel seems to cease syneresis after 4 to 6 days. The 3 normal acid gel completes its syneresis after 12 days. A noticeable decrease in firmness occurs after 8 days in the 6 normal acid gel but not in the 3 normal acid gel.	No furtner study on shrinkage at this time but time of syneresis reduction should be noted. Note warping and cracking from uneven drying in following experiments.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-31 (con.)		H-2071.2 432 g cellulose acetate (Type E-394-30) 1440 cc 3 N H^+ and 1 M NO_3^-	Same as H-2071.1.	After 4 days gel was removed from tray. 280 cc of acid had been extruded and a shrinkage of 7/8 inch in 12 inches had occurred. After 8 days an additional 140 cc of acid had been extruded but no further shrinkage was noted. The gel surface was still damp with acid. After 12 days the gel had extruded an additional 40 cc of acid but still no further shrinkage. A total of 460 cc of acid extruded in 12 days with only 15 g of total weight unaccounted for. Loss probably due to evaporation. This gel is still very firm after 12 days.		
H-32	To prepare a gel typical of type to be used in eventual application of cutting honeycomb.	H-2107.1 288 g cellulose acetate (Type E-394-30) 960 cc 6 N H^+ and 2 M NO_3^-	Mix for 2 minutes in air blender at medium speed and cast as long flat strip. Mold dimensions 18 x 4 x 3/4 inches. Remove gel after 24 hours from mold and allow to stand uncovered in hood.	Gel firm when removed from mold. After 2 days uncovered in hood gel has become warped and cracking is present on gel surface. During an additional 4 days gel warped severely and cracked to an extent that gel was severed in several places. Total shrinkage during period was 1.5 inches in 18 inches.	This experiment shows that relatively large gels are entirely feasible using the cellulose-acetate gel system. Also, it was pointed out how important a controlled drying period is in the prevention of destructive warping and cracking of gels.	No further investigation with gels of this size planned at this time.
		H-2107.2 Same as H-2107.1.	Same as H-2107.1 except that gel is kept covered in mold with drains to remove extruded acid.	After a total period of 2 weeks in covered mold no warping or cracking took place. Total shrinkage was 3/4 inch in 18 inches. When removed from mold, surface was extremely flat, almost a mirror finish.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-33	To investigate cellulose-acetate gels made with acid concentrations between 3 and 6 normal.	H-2075.1 432 g cellulose acetate (Type E-394-30) 1440 cc 5 N H^+ and 1.66 M NO_3^- H-2075.1 432 g cellulose acetate (Type E-394-30) 1440 cc 4 N H^+ and 1.33 M NO_3^-	Blend for 2 minutes in air blender at medium speed and cast as flat section in tray.	Both gels were observed noting syneresis, firmness, shrinkage, and honeycomb finishes produced. The two gels appear to have no outstanding properties that would naturally fall between the range of the 6 normal and 3 normal acid gels used previously.	No outstanding results were found from this experiment.	No further study planned at this time.
H-34	To cut a 17-7PH honeycomb sample using a cellulose-acetate gel 12 days old.	36 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Place two honeycomb samples over gel with 15 g weight per 1 square inch and allow honeycomb to "walk in". After 12 days this gel is not as firm as directly after gelation.	After 19 hours a cut of approximately 1/8 inch had been made. Gel surface was dry but honeycomb core was embedded slightly in the gel making the finish uneven. A red oxide coating was present on the honeycomb with its highest concentration where the "walk in" weights were placed blocking the ventilation. Where this oxide film was concentrated, pin holes were made in the honeycomb wall section.	To give proper finishes oxide film must be lessened. A more rapid cutting time or proper ventilation or both must be provided.	Further study planned. Electrolytic application is the most convenient way to decrease the cutting time.
H-35	To investigate the electrolytic etching characteristics of cellulose-acetate gels after syneresis is essentially completed.	36 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Gel has been kept in closed container for 14 days after mixing. Place honeycomb core over gel with 15 g weight per 1-square inch area and apply potential across gel making honeycomb anodic.	time = 0, i = 0.43 ampere V = 2.75 volts Initial reaction products were brown. time = 60 minutes i = 0.53 ampere, V = 2.3 volts time = 90 minutes i = 0.53 ampere, V = 2.25 volts Honeycomb removed after 90 minutes. Finish was not perfectly flat, showing anodic and cathodic areas. Indentations were present at welded junctions. Gel surface was not dry with liquid at contact points of honeycomb. Slight embedding of honeycomb into gel. The reaction products turned from brown to green after standing for 24 hours.	Liquefication at gel surface is detrimental to finish. Must be eliminated to give good surface on honeycomb.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-36	Repeat Expt. H-35 using more firm gel and lower current.	36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-	Same as Expt. H-35.	time = 0, i = 0.2 ampere V = 2.5 volts time = 60 minutes i = 0.23 ampere, V = 2.15 volts Finished surface was uneven primarily due to warped honeycomb sample. Where gel was in good contact with honeycomb reaction products were brown and liquefication was very slight. Where the gel and the honeycomb were in poor contact the reaction products were green and liquefication on the gel surface was very prominent.	Liquefication still present on gel surface.	Reduce current further and/or allow gel to dry (uncovered) for 12 hours.
H-37	Repeat Expt. H-36 reducing current.	Same as Expt. H-36.	Same as Expt. H-36.	time = 0, i = 0.1 ampere V = 2.0 volts Reaction products are green. time = 60 minutes i = 0.11 ampere, V = 1.8 volts time = 120 minutes i = 0.11 ampere, V = 1.9 volts time = 180 minutes i = 0.11 ampere, V = 1.95 volts Finish was uneven, again probably due to slight warpage of gel and honeycomb. Depth of cut was approximately 10 mils. Gel surface was again covered with thin liquid film at contact points of honeycomb.	The liquid film is still present even with this low current.	To lower the current more would result in a very small cutting rate. Additional weight might be used to make cut more even.
H-38	Perform an electrolytic cut increasing "walk in" weight, current, and allowing H-35 gel to "dry" an additional 12 hours uncovered.	Same as Expt. H-35.	Same as Expt. H-35 except use 50 g weight per 1-square inch honeycomb area.	time = 0, i = 0.90 ampere V = 3.5 volts time = 20 minutes i = 0.89 ampere, V = 3.65 volts time = 40 minutes i = 1.04 amperes, V = 3.7 volts Reaction products were very dark and diffused 3/8 inch in 40 minutes. Finish showed anodic and cathodic areas with indentations at welded junctions. 25 mils were removed in the 40-minute etching time. Gel surface had liquid film at contact points of honeycomb.		Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-39	To make a cut in 17-7PH S.S. honeycomb core 0.025-inch deep using apparatus with stops.	36 g cellulose acetate (Type E-394-30) 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^-	Gel 8-days old which had been uncovered 4 days prior to use. Honeycomb area approximately 4-square inches. 60 g weight used for "walk in" technique.	After a total time of 20 hours the honeycomb had reached the stops. Finish was flat except for several large areas where gas was entrapped under gel surface and caused raised areas on gel. Depth of cut approximately 30-33 mils in areas void of raised portions of gel.	Raised parts of gel must be eliminated before flat finishes can be made. Gas entrapment may be due to slight embedding of honeycomb in gel.	Initial elimination of gas at gel surface can be made by using electrolytic approach.
H-40	Repeat Expt. H-39 except use electrolytic approach.	Same as Expt. H-39.	Same as Expt. H-39.	Gel surface initially dry when voltage applied. time = 0, i = 0.6 ampere V = 0.45 volts Immediate rise in voltage. time = 1 minute i = 0.5 ampere, V = 1.5 volts Liquefication on gel surface. Reaction products dark brown, becoming green as they diffuse through gel. time = 45 minutes i = 0.49 ampere, V = 1.55 volts time = 60 minutes i = 0.48 ampere, V = 2.0 volts Sample reached stop on one side. Rise in voltage may be due to less contact area now. time = 85 minutes i = 0.58 ampere, V = 1.98 volts Both stops in contact. Honeycomb removed. Liquid film present on gel where honeycomb contacted. Slight cracking of gel. Surface finish was slightly scalloped. Depth of cut was 0.025 $\pm$ 0.003 inch.	Results show that stops are feasible as a method of gaging depth of cut.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-41	Repeat Expt. H-40 except allow gel to dry an additional day uncovered in hood.	Same as Expt. H-40.	Same as Expt. H-40 except gel 7 days old.	time = 0, i = 0.4 ampere V = 1.8 volts time = 30 minutes i = 0.37 ampere, V = 2.2 volts At 50 minutes, current was zero due to poor contact in circuit. Circuit repaired and at time = 51 minutes i = 0.5 ampere, V = 0.6 volts time = 60 minutes i = 0.4 ampere, V = 1.9 volts time = 90 minutes i = 0.4 ampere, V = 1.9 volts time = 97 minutes i = 0.4 ampere, V = 1.9 volts Honeycomb sample reached stops. Gel surface again was wet and had cracked. Finish was slightly scalloped with nodes at welded junctions. Depth of cut was approximately 20 mils to nodes and 25 mils to low parts of scalloping.	Liquid forms on gel surface either as a result of increased syneresis due to heating of gel or due to reaction when etching. Liquid film on gel is undesirable as well as surface cracking of gel.	Experiments should be performed in an effort to eliminate liquid film or gel cracking.
H-42	To electrolytically etch a 17-7PH honeycomb core using an extremely old gel in an effort to try to distinguish between liquid on gel formed due to syneresis or reaction products.	36g cellulose acetate (Type E-394-30) 120cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Gel 18 days old. Apply voltage in same manner as Expt. H-40.	time = 0, i = 0.35 ampere V = 2.75 volts time = 10 minutes i = 0.34 ampere, V = 2.7 volts time = 20 minutes i = 0.36 ampere, V = 2.65 volts No visible liquefication on gel surface yet. Reaction products have been brown. time = 30 minutes i = 0.36 ampere, V = 2.65 volts time = 50 minutes i = 0.36 ampere, V = 2.5 volts time = 60 minutes i = 0.37 ampere, V = 2.5 volts Slight liquid film visible on gel surface now.	Cracking of gel not present with this gel formulation. Liquid film still present but delayed in formation.	Further study with different gel formulation needed.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-42 (con.)				time = 90 minutes $i = 0.36$ ampere, $V = 2.75$ volts time = 120 minutes $i = 0.36$ ampere, $V = 2.75$ volts Liquid film on gel, however, no cracking present. Anodic and cathodic areas present on honeycomb surface. Depth of cut 30-35 mils.		
H-43	Repeat Expt. H-42 using gel made with 6-normal H^+ ion and 2-molar NO_3^- ion acid.	36 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Same as Expt. H-42 except gel 16 days old. Gel of mushy texture.	time = 0, $i = 0.4$ ampere $V = 2.0$ volts time = 15 minutes $i = 0.44$ ampere, $V = 1.75$ volts Experiment interrupted due to accident with apparatus. Gel surface cracked and liquid film present on gel. Finish appears to be approaching a scalloped finish.	Even though experiment was interrupted, 6-normal H^+ ion and 2-molar NO_3^- ion acid gels seem to have undesirable qualities for electrolytic etching.	For further electrolytic cuts, 3-normal H^+ ion and 1-molar NO_3^- ion acid gel formulations recommended.
H-44	To nonelectrolytically etch a honeycomb sample using 6-normal acid gel. Depth of cut desire 0.025 inch. Stop apparatus to be used.	36 g cellulose acetate (Type E-394-30) 120 cc 6 N H^+ and 2 M NO_3^-	Gel 8 days old with initial dry surface. Place honeycomb over gel with 15 g weight per square inch honeycomb area.	After 14-hour cutting period, gel reached stops. No raising of gel due to entrapped air this time. Contact between gel and honeycomb was uneven. Where good contact present, no liquid film; at poor contact areas, heavy liquid film. Finish was uneven with 25 mils removed where good contact was present between gel and honeycomb.		6-normal acid gels seem to give irregular results which distract from their usefulness.
H-45	Repeat Expt. H-44 using 3-normal acid gel.	36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-	Gel 12 days old. Kept covered since mixing.	After a 20-hour period apparatus has reached stops. Gel warpage has caused uneven cut with areas of good and poor contact between gel and honeycomb core. Again, where poor contact, large amount of liquid on gel surface.	Liquid where poor contact present is presumably due to acid not being used up as it is slowly extruded from gel. Acid extrusion does not appear to completely stop even for very old gels, but amount extruded is reduced so that it is used (or evaporates) at a rate equal to or greater than extrusion rate.	Long cutting periods require a flat gel over cutting period. With this gel system warping is difficult to eliminate. Further emphasis on electrolytic cutting should be applied.

APPENDIX D (Continued)

Expt. No	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-46	To electrolytically etch a 17-7PH S.S. honeycomb sample 0.025 inches. Using a stop apparatus.	36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ ion and 1 M $N)_3^-$ ion acid.	Adjust stops 0.025 inches below gel surface. Place approximately 200 g weight for 4 sq inches honeycomb area. Gel 14 days old when used.	time = i = 0.15 ampere V = 2.2 volts Reaction products were brown. time = 15 minutes i = 0.3 ampere V = 1.9 volts time = 30 minutes i = 0.3 ampere V = 1.9 volts time = 45 minutes i = 0.29 ampere V = 1.95 volts time = 60 minutes i = 0.29 ampere V = 1.90 volts time = 65 minutes i = 0.29 ampere V = 1.95 volts Sample reached stops after 65 minutes. Depth of cut was 15 mils with flat surface produced. Slight anodic and cathodic areas were produced. Gel surface was damp at contact points of honeycomb.	Flatness of surface indicates possibility of producing acceptable cuts electrolytically.	Further study planned.
H-47	To produce 0.025 inch cut as in expt. H-46.	Same as H-46	Same as H-46 except stops set at 0.030 inches.	time = 0 i = 0.18 ampere V = 2.1 volts time = 60 minutes i = 0.18 V = 2.0 volts Reaction products were very dark green. time = 120 minutes i = 0.18 ampere V = 2.2 volts time = 145 minutes i = 0.17 ampere V = 2.4 volts Uneven surface finish produced due to poor apparatus alignment. Gel surface was damp at honeycomb contacts. Liquid on gel surface evaporated within 2 minutes after removal of honeycomb.		Try increased current experiment.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-48	To electrolytically etch 17-7PH honeycomb core using higher current than in H-47.	Same as H-47.	Same as H-47 except increase current and add additional 500 g weight.	time = 0, i = 0.78 ampere V = 3.1 volts time = 10 minutes i = 0.84 ampere, V = 2.8 volts Reaction products were brown. time = 20 minutes i = 0.82 ampere, V = 2.8 volts time = 35 minutes i = 0.8 ampere, V = 3.0 volts Sample reached stops after 35 minutes. Gel surface had liquid layer at contact points of honeycomb. The honeycomb finish was very flat and was approximately 25 mils deep, the desired depth. Surface had slight projections at welded junctions.	From initial results a flat 25-mil cut is entirely possible using a current density of approximately 0.8 ampere for 4 square inches of honeycomb area. Increased weight tended to decrease apparatus binding as "walk-in" proceeded.	Further study planned to see if results are readily reproducible.
H-49	To prepare a cellulose acetate gel using Acid M-2528. This acid in CMC gels forms no liquid	36 g cellulose acetate (Type E-394-30) 120 cc Acid M-2528 Acid formation: 70 ml H_2O 30 ml HF 25 g $NiCl_2 \cdot 6H_2O$ 3.5 g Na_2SO_4	Add cellulose acetate to acid and mix for 2 minutes at medium speed with air blender. Cast in petri dish.	Mixture had initial separation of acid 1/8-inch thick at bottom of petri dish. Gelation time was within 60 hours. Gel was slightly mushy, but syneresis had not occurred in 60 hours.	Cellulose acetate gels using Acid M-2528 are possible.	Etching tests will be performed. Further improvement of gel may be investigated.
H-50	To investigate electrolytic properties of gel prepared in Expt. No. H-49.	Same as H-49.	Due to mushy texture of gel, it was not removed from petri-dish mold. Place 17-7PH S.S. honeycomb in center of dish with two cathodes on either side of honeycomb embedded in gel. Apply potential across gel making honeycomb anodic.	time = 0, i = 0.38 ampere V = 2.4 volts time = 30 seconds i = 0.47 ampere, V = 1.7 volts time = 15 minutes i = 0.38 ampere, V = 2.8 volts time = 45 minutes i = 0.34 ampere, V = 2.95 volts time = 50 minutes i = 0.33 ampere, V = 3.05 volts Sample was removed after 50 minutes. Liquefaction and embedding of honeycomb was present at gel surface. Honeycomb finish was scalloped.	Etching characteristics of this gel are not favorable for honeycomb core.	Repeat this experiment using flat plate as anode to see if liquid forms at anode. If no liquid forms, investigate similar formulations.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-51	To repeat H-50 using flat plate an anode.	Same as H-49	Same as H-50 except use Inconel X flat plate as anode.	time = 0, i = 0.50 ampere V = 1.15 volts time = 35 minutes i = 0.53 ampere, V = 1.13 volts time = 60 minutes i = 0.53 ampere, V = 1.09 volts Sample removed from gel after 60 minutes. No liquefication was present however gel adhered to sample. Gel surface seemed to crystallize slightly.	No liquid present at anode surface warrants further study.	Further study in area of gel formulation planned.
H-52	To investigate cellulose acetate gels made with formulations similar to H-49.	H-2130.1 36 g cellulose acetate (Type E-394-30) 110 cc Acid M-2528 10 cc hydrochloric acid 20° Be	Mix both for 2 minutes at medium speed in air blender and cast in individual petri dishes.	There was an initial acid separation with both mixtures. After 20 hours both had gelled. H-2130.1 was less firm than H-2130.2. No syneresis present yet.	Gel behavior is similar to normal cellulose acetate gels.	Since syneresis exists, try formulations using essentially normal cellulose acetate gel mixtures with additives. Investigate etching characteristics of H-2130.1 and H-2130.2 gels.
		H-2130.2 36 g cellulose acetate (Type E-394-30) 110 cc Acid M-2528 10 cc nitric acid 38° Be		After 72 hours, gel H-2130.2 was extruding acid. H-2130.1 gel was more firm with no syneresis. After 96 hours, both gels were extruding acid.		
H-53	To evaluate electrolytic etching characteristics of gels made in Expt. No. H-52.	Test Run No. 1, H-2130.1.	Electrolytically cut a 17-7PH S. S. sample by method previously used (i.e. allow honeycomb to "walk-in" from above).	time = 0, i = 0.35 ampere V = 4.5 volts time = 20 minutes i = 0.32 ampere, V = 4.7 volts time = 35 minutes i = 0.23 ampere, V = 5.8 volts Sample removed after 35 minutes. Cut slightly scalloped. Liquid film on gel surface.	These two gels have very high resistance initially which increases as the cutting time increases. Cut for either gel is not satisfactory.	No further study planned.
		Test Run No. 2, H-2130.2	Same as Test Run No. 1.	time = 0, i = 0.55 ampere V = 4.75 volts time = 20 minutes i = 0.18 ampere, V = 11.4 volts Sample removed after 20 minutes due to drastic resistance increase. Cut depth was negligible. No liquid on gel surface but crystal-like structure present at anode contact points.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-54	Observe cellulose acetate gels with 3 N H^+ and 1 M NO_3^- acid as the principle acid ingredient, but also containing sodium sulfate, nickelous chloride, and hydrofluoric acid.	H-2133.1 36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^- acid 15 g $NiCl_2 \cdot 6H_2O$ 3 g Na_2SO_4 H-2133.2 36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^- acid 10 cc hydrofluoric acid 52-55% 15 g $NiCl_2 \cdot 6H_2O$ 3 g Na_2SO_4	Mix each formulation for 2 minutes at medium speed in air blender and cast in petri dishes.	An initial separation of 1/8-inch acid at bottom of petri dish occurred. The mixtures gelled firmly within 36 hours but began to syneresis following firm gelation. After 6 days the gels shrank 3/4-inch in 5-1/2 inches.	Severe shrinkage accompanied by poor etching characteristics observed in Expt. H-53 (crystallization at anode surface presumably due to nickelous chloride) indicates gels unsatisfactory.	No further study planned.
H-55	Investigate cutting characteristics of cellulose acetate gels 6 days after preparation on 17-7PH S.S. honeycomb. Use electrolyte means.	36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^- acid	Gel used 6 days after preparation. Allow gel to dry in still air 1 hour prior to use. Place an apparatus and set stops at 0.030 inch. Use 500 g weight atop honeycomb for 5 sq inches of cutting area.	time = 0, i = 0.78 ampere V = 2.4 volts Reaction products was yellow-brown. time = 10 minutes i = 0.84 ampere, V = 2.5 volts time = 25 minutes i = 0.83 ampere, V = 2.6 volts time = 35 minutes i = 0.81 ampere, V = 2.6 volts Honeycomb reached stops after 35 minutes. A heavy liquid film was present on gel surface. Honeycomb finish had slight anodic and cathodic areas at welded junctions but otherwise were quite flat. Depth of cut was 0.025 ± 0.001 inch.	Liquid film forming at anode surface results in pronounced anodic and cathodic areas.	Either allow additional drying time prior to use or additional period before use.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-56	Repeat Expt. H-55 allowing an additional drying time prior to use.	Same as H-55	Same as H-55 except allow 2 hours drying time prior to use.	time = 0, i = 0.8 ampere V = 2.7 volts Reaction products were brown. time = 10 minutes i = 0.81 ampere, V = 2.7 volts time = 20 minutes i = 0.81 ampere, V = 2.7 volts time = 30 minutes i = 0.82 ampere, V = 2.7 volts Stops were reached after 30 minutes. Gel surface was again damp but to a lesser degree than H-55. Surface finish was better than previous experiment. Depth of cut was 21 mils. Slight projections at welded junctions were 2 mils high above rest of surface.	A relatively flat surface was obtained by the procedure used in this experiment. However, it should be investigated as to the effect of a longer aging period after mixing.	Further study planned.
H-57	Investigate 17-7PH S.S. honeycomb finishes obtained from cellulose acetate gels used 10 days after mixing.	36g cellulose acetate (Type E-394-30) 120 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^- acid	Use gel prepared 10 days in advance. Allow 1 hour drying period in still air prior to use. Place gel and honeycomb in apparatus and utilize electrolytic "walk in" technique. 500 g weight placed atop honeycomb.	time = 0, i = 0.80 ampere V = 2.9 volts Brown reaction products. time = 10 minutes i = 0.87 ampere, V = 2.75 volts time = 25 minutes i = 0.74 ampere, V = 3.75 volts time = 35 minutes i = 0.71 ampere, V = 3.75 volts Gel surface was slightly damp, much less than 6-day gels. Honeycomb surface was very flat with slight projections at welded junctions. Very slight anodic and cathodic areas observed around welded junctions. Depth of cut was 0.020 $\pm$ 0.001 inch.	A 10-day period after mixing seems to result in good cuts as far as surface finishes for shallow cuts.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-58	Repeat Expt. H-57 using gel 11 days old.	Same as H-57	Same as H-57 except gel 11 days old.	time = 0, i = 0.8 ampere V = 2.8 volts Brown reaction products. time = 10 minutes i = 0.8 ampere. V = 2.65 volts time = 20 minutes i = 0.79 ampere, V = 2.75 volts time = 30 minutes i = 0.77 ampere, V = 2.8 volts time = 35 minutes i = 0.77 ampere, V = 2.8 volts Gel finish very similar to that of Expt. H-57. When the projections were removed with a regular finishing file, the cut was 0.025 + 0.001 inches.	The results of electrolytic etching of 17-7PH S.S. honeycomb core using 3-1 acid gels indicate the feasibility of this system for accurately cutting honeycomb on a laboratory scale. An important point is the uniformity of the cuts. Thus reproducibility does not seem to be a major problem at the present time.	No further study planned in immediate future.
H-59 Run No. 1	To electrolytically etch a 302 S.S. sample using a cellulose-acetate gel placed in an acid bath.	24g cellulose acetate (Type E-394-30) 120cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Use gel 3 days after preparation. Gel placed in petri dish and sample placed atop gel. Acid used in gel preparation placed in petri dish with acid surface approximately 1/4 inch from S.S. sample. Cathode of 302 S.S. placed in bath. Voltage applied across gel making sample to be etched anodic. Replace gel and sample after each run.	Gel surface area 2.5 sq in. time = 0, i = 0.53 ampere V = 0.65 volt Black film at anode. Reaction products green. time = 1 hour i = 0.46 ampere, V = 0.68 volt time = 2 hours i = 0.46 ampere, V = 0.65 volt time = 3 hours i = 0.46 ampere, V = 0.64 volt time = 3-1/2 hours i = 0.48 ampere, V = 0.62 volt Shiny surface finish. Many small areas where no etch at all. Groove is present around gel contact area where etch quite severe. Depth of groove is approximately 7 mils. Contact area of gel etched 1 mil. Gas entrapment in gel gave blister effect at surface. Reaction products diffused to plane where acid separation occurred on gelling. Little or no diffusion beyond.	Blistering of gel surface and deep grooving around perimeter of gel contact area are immediate problems with this system and procedure.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-59 (con.) Run No.2				Gel area 2 sq in. time = 0, i = 0.70 ampere V = 0.67 volt Reaction products green. Black film at anode surface. time = 1 hour i = 0.65 ampere, V = 0.86 volt time = 2 hours i = 0.67 ampere, V = 0.87 volt Acid reservoir renewed after 2 hours. time = 2.5 hours i = 0.97 ampere, V = 0.67 volt Run stopped due to acid meniscus over sample surface. Cut similar to Run No. 1. Gel blistering present again. Increased current produced no visible changes in sample finish. Again products were retarded at plane where gel separation occurred.		
H-60 Run No. 1	To electrolytically etch a 302 S.S. sample over an extended period of time using reservoir technique as in H-59.	Same as H-59	Same as H-59 except for Run No. 2, use gel and sample of Run No. 1.	Gel area 2.5 sq in. time = 0, i = 0.74 ampere V = 0.72 volt Reaction products green. Black film at anode. time = 2.5 hours i = 0.65 ampere, V = 0.85 volt Acid bath changed. time = 2.5^{+} hours i = 0.59 ampere, V = 0.94 volt Green reaction products. time = 16 hours i = 0.13 ampere, V = 1.8 volts The acid reservoir is very dark green, almost opaque. Groove present around cut 10-12 mils deep. Gel contact area etched 3 mils. Finish was slightly mottled.	Grooving still present with this experiment. Conditions leading to brown reaction products and corresponding etch should be investigated.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-60 (con.) Run No. 2				Use gel and sample of Run No. 1. time = 0, i = 0.78 ampere V = 2.0 volts Reaction products are yellow-brown. No visible black film at anode surface. time = 1 hour i = 0.69 ampere, V = 2.2 volts time = 2 hours i = 0.67 ampere, V = 2.3 volts Reaction products continued to be brown. Depth of cut increased from 3 mils to 5 to 7 mils. Grooving still present but decreased slightly. Product diffusion negligible past acid separation plane.		
H-61	To repeat extended run in Expt. H-60.	Same as H-60	Same as H-60 except Run No. 1 only performed.	Gel area 2 sq in. time = 0, i = 0.58 ampere V = 0.70 volt Green reaction products. time = 16 hours i = 0.20 ampere, V = 1.36 volts Run stopped after 16 hours. Bath is very dark green, almost opaque. Gel surface covered with black film. Finish of 302 S.S. sample is very mottled. Grooved perimeter again present. Depth of cut 7 to 9 mils on gel surface area and 25 mils in grooves.	Prohibiting factors seem to be film on gel surface which seems to contribute to a mottled surface and extreme grooves around gel perimeter.	Grooved perimeter may be due to current concentration around gel. This may be reduced by placing cathode beneath gel during etching.
H-62	To etch a 302 S.S. sample by the reservoir technique with the cathode beneath the gel.	24 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 $\underline{\bar{M}}$ NO_3^-	Gel 6 days old when used. Use previous reservoir technique but place cathode beneath gel.	Gel area 2 sq in. time = 0, i = 0.52 ampere V = 0.47 volt Green reaction products. time = 14 hours i = 0.04 ampere, V = 0.95 volt Bath is very dark green. There seems to be no improvement over method previously used with cathodes on either side of gel. Less metal seems to have been removed than previous experiments.	Cathode under gel does not seem to reduce problems of grooving or of poor surface finishes.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-63	To reproduce conditions which led to brown reaction products in H-60.	36 g cellulose acetate (Type E-394-30) 120 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Place gel in petri dish and add acid reservoir. Use general procedure of previous reservoir experiments except use two cathodes. One on either side of gel.	Gel area 1/2 sq in. time = 0, i = 0.63 ampere V = 2.0 volts Reaction products brown. time = 1 hour i = 0.4 ampere, V = 2.5 volts time = 2 hours i = 0.35 ampere, V = 2.6 volts time = 3 hours i = 0.32 ampere, V = 2.7 volts Finish slightly mottled with groove around contact area. Depth of cut on gel area is 3 to 5 mils. Very viscous liquid layer on gel surface.	A faster etch rate seems to accompany brown reaction products.	Further study planned.
H-64	To try to determine the causes of the different colored reaction products formed.	24 g cellulose acetate (Type E-394-30) 120 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Gel used 5 days after preparation. Drying period of 1 hour prior to use allowed. Gel placed in reservoir and voltaged applied as before.	Gel area 1/4 sq in. time = 0, i = 0.48 ampere V = 1.5 volts Reaction products are green. This implies that dry gel surface does not cause brown products. Voltage increased. Current increased correspondingly and then dropped off quickly with further increase in voltage. Resistance of cell increased from 3 ohms to 5 ohms. time = 1 minute i = 0.49 ampere, V = 2.65 volts time = 10 minutes i = 0.46 ampere, V = 2.75 volts Brown reaction products. time = 35 minutes i = 0.42 ampere, V = 2.85 volts time = 80 minutes i = 0.36 ampere, V = 3.0 volts time = 120 minutes i = 0.24 ampere, V = 3.2 volts Brown reaction products continue. Cut and depth of cut similar to previous experiments.	Brown reaction products seem to form when the current density reaches a certain value. The acid seems to deplete more rapidly when brown products are formed.	No appreciable difference in gel performance for either type of reaction product. No further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-65	To electrolytically etch a 302 S.S. sample using only portion of gel below acid separation that occurs on gelling.	24 g cellulose acetate (Type E-394-30) 120 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Gel used 3 days after preparation. Use only section of gel below separation. Use reservoir technique but increase separation between acid surface to 3/8 inch.	Gel area = 2 sq inches. time = 0, i = 0.60 ampere V = 0.80 volt Green reaction products. time = 35 minutes i = 0.48 ampere, V = 0.85 volts time = 1 hour i = 0.44 ampere, V = 0.88 volt time = 2 hours i = 0.41 ampere, V = 0.90 volt Dry area between anode surface and reservoir surface. time = 3 hours i = 0.44 ampere, V = 0.87 volt Reservoir becoming noticeably green. time = 4 hours i = 0.40 ampere, V = 0.88 volt A definite demarcation exists between product diffusion and acid reservoir surface. Gel surface has a liquid film present. Finish is uneven with several large areas where no etch occurred. Groove around perimeter of gel approximately 4 mils deep. Gas bubbles being emitted from gel surface.	Diffusion seems to be increased by using only lower portion of gel below separation. Surface improvement is not significant.	Further study planned.
H-66	Using etched sample of Expt. H-61, repeat etch in same manner to note changes in surface finish produced.	24 g cellulose acetate (Type E-394-30) 120 cc 3 $\underline{N}$ H^+ and 1 $\underline{M}$ NO_3^-	Gel used 4 days after preparation. Use procedure of H-65.	Gel area 2 sq in. time = 0, i = 0.40 ampere V = 1.87 volts Brown reaction products. Resistance of cell varies with voltage Voltage Current Resistance 0.22 0.01 22 0.46 0.017 27 0.70 0.018 39 0.95 0.019 50 1.20 0.022 54.5 1.37 0.050 27.4	Gel surface is not improved appreciably. A series of shorter runs may be required for surface improvement.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-66 (con.)				Voltage / Current / Resistance 1.55 / 0.122 / 12.7 1.72 / 0.240 / 7.2 1.78 / 0.305 / 5.6 1.90 / 0.402 / 4.7 Experiment allowed to continue. time = 13.5 hours i = 0.245 ampere, V = 2.05 volts Green products now. Depth of cut increased to 14 mils. Groove is approximately 30 mils deep. Surface shows slight improvement.		
H-67 Run No. 1	To etch 302 S.S. sample of Expt. H-66 for a series of short runs.	24 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-	Gel prepared 5 days prior to use. Use same reservoir technique of H-66 except use whole gel and not just portion below separation. For each run replace gel and acid reservoir.	Gel area 2 sq in. time = 0, i = 0.40 ampere V = 1.6 volts Brown reaction products. time = 1 hour i = 0.37 ampere, V = 1.83 volts time = 2 hours i = 0.38 ampere, V = 1.85 volts time = 3-1/4 hours i = 0.35 ampere, V = 1.85 volts Surface finish improved. Surface depth is 16 mils. Groove is not as severe.	Sample surface seems to be improved when products are being diffused away at a fairly rapid rate. Once the rate is slowed down the surface becomes undesirable.	Gels without separation on gelation may improve surface finish and depth of cut.
Run No. 2				time = 0, i = 0.4 ampere V = 2.8 volts Voltage decreased to zero and then increased. Current increased to approximately 0.3 ampere with corresponding increase in voltage to approximately 0.6 volts. Above 0.6 volts the current dropped to essentially zero and then increased after the voltage was 1.5 volts to initial conditions. This phenomenon was repeated twice more with same results. The third time the current was increased above 0.8 ampere without dropping. Run then continued.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-67 Run No. 2 (con.)				i = 0.4 ampere, V = 0.54 volts Green reaction products. Brown products presumed to accompany high resistance cell. time = 1 hour i = 0.31 ampere, V = 0.59 volts time = 2.5 hours i = 0.26 ampere, V = 0.60 volts Depth of surface 19 mils. Groove 35 mils. No surface change.		
Run No. 3				time = 0, i = 0.80 ampere V = 1.00 volt Green reaction products. Unsuccessful attempt made to reproduce results of Run No. 2. time = 1-1/2 hours i = 0.17 ampere, V = 1.40 volts Surface depth 22 mils. General smoothing of surface observed.		
Run No. 4				time = 0, i = 0.80 ampere V = 0.84 volt Green products. time = 1 hour i = 0.54 ampere, V = 0.95 volt Surface depth 24 mils. Continued smoothing.		
Run No. 5				time = 0, i = 0.81 ampere V = 0.80 volt Green products. time = 1 hour i = 0.55 ampere, V = 0.95 volt Surface depth now 27 mils. Groove smoothed slightly. In all cases of short runs products diffused through gel to plane of gelling separation. At this plane a resistance to diffusion was noted. All gels seemed to emit gas when removed from reservoir.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-68	To investigate electrolytic etching characteristics of gel formulated to eliminate separation on gelation.	24 g cellulose acetate (Type E-394-30) 60 cc 6 $\underline{N}$ H^+ and 2 $\underline{M}$ NO_3^- 60 cc Methanol 20 cc dibutylphthalate	Use gel 3 days after preparation. Place 4 inches x 4 inches 302 S.S. sample atop gel in petri dish with acid reservoir. Apply voltage in usual manner.	Gel area 2 sq inches time = 0 i = 0.40 ampere V = 0.67 volts Green reaction products time = 1 hour i = 0.26 ampere V = 0.69 volts time = 2.5 hours i = 0.22 ampere V = 0.72 volts Slight liquid film on gel surface. Depth of cut was not measurable but product diffusion seemed to be as rapid or more rapid than separating gels. Finish uniform with only slight grooving around gel perimeter.	Gel diffusion and surface finish seems to be improved. Depth of cut however was small and must be improved.	Increase current in effort to make deeper cut.
H-69	Repeat expt. H-68 using higher current density.	Same as H-68	Same as H-68	Gel area 2 sq incyes time = 0 i = 1.0 ampere V = 1.32 volts Brown reaction products time = 30 minutes i = 0.28 ampere V = 1.85 volts time = 60 minutes i = 0.26 ampere V = 1.85 volts Voltage increased to 2.5 volts i = 0.73 ampere V = 2.5 volts time = 120 minutes i = 0.59 ampere V = 2.60 volts Gassing at the cathode was not increased when voltage was increased. time = 150 minutes i = 0.48 ampere V = 2.74 volts Gel and sample similiar to sample of H-67. Depth of cut was again shallow with increased grooving.	This gel formulation seems to produce relatively good finishes with little depth.	No further study planned.

APPENDIX D (Continued)

Expt. No	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-70	To electrolytically etch a 302 S.S. sample using a gel situated in reservoir in such a manner to allow diffusion from the bottom of the gel.	24 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-.	Use gel prepared 8 days prior. Use only section of gel below separation. Place gel on flat circular porous sand casting in petri dish. Fill petri dish with acid until surface of reservoir is even with sand casting surface. Place sample on gel and apply potential. Use a cathode on either side of gel.	Gel thickness 1/8 inch. time = 0 i = 0.50 ampere V = 1.40 volts Green reaction products. time = 35 minutes i = 0.44 ampere V = 1.44 volts Products had diffused almost completely through gel. Reservoir becoming colored with products. time = 2-1/2 hours i = 0.42 ampere V = 1.45 volts time = 3-1/2 hours i = 0.30 ampere V = 1.72 volts time = 5 hours i = 0.18 ampere V = 1.74 volts Surface finish was quite rough with little depth. Numerous high spots where etch seemed negligible. Grooving was very slight. No damage to gel during experiment.	Although diffusion appeared to be good, no appreciable etch was produced. Grooving was not a problem.	Further study planned.
H-71	Repeat expt. H-70 with a few alterations.	Same as H-70.	Same as H-70 except pickle sample in concentrated HCl for 20 minutes prior to placing on gel.	Gel thickness was 1/8 inch area was 2 sq inches. time = 0 i = 0.80 ampere V = 0.95 volts Green reaction products time = 30 minutes i = 0.67 V = 1.05 volts time = 80 minutes i = 0.14 ampere V = 1.55 volts Increase voltage. i = 0.80 ampere V = 2.35 volts Liquid film formed at anode surface which intermittently flowed to acid reservoir. Slight anodic gassing observed.	Due to no contact area the current density was higher than desired and therefore products were produced too rapidly for proper diffusion.	Continue experiment using new acid reservoir. Use sample and gel of this experiment.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-71 (con.)				time = 4 hours i = 0.69 ampere V = 2.45 volts time = 6 hours i = 0.67 ampere V = 2.50 volts Surface finish was slightly mottled with an area of no etch. No etch area due to contour of gel surface. Depth of cut where etch present was 4 mils.		
H-72	Rerun H-71 replacing acid reservoir o[illegible]	Same as H-71.	Same as H-71.	time = 0 i = 0.82 ampere V = 2.3 volts Green reaction products. time = 3 hours i = 0.72 ampere V = 2.4 volts Replace acid reservoir. i = 0.74 ampere V = 2.4 volts time = 13-1/4 hours i = 0.61 ampere V = 2.45 volts Reservoir was very dark green, almost opaque. A slight attack on the cathodes had taken place. Gel surface was covered by a relatively thick layer of reaction products. Finish was mottled. Product layer reflected surface finish. Depth of etch was increased to 10 mils.	Reaction products forming on gel surface seem to be the major cause of the poor surface finishes.	Further investigation planned.
H-73 Run No. 1	Rerun experiment H-71 allowing gel to be used only for periods of 4 hours.	Same as H-71	Same as H-71 except pickle in concentrated HCl for 5 minutes. Rep.ace gel and acid reservoir for each run. Keep current essentially constant.	Gel area 1 sq inch. time = 0 i = 0.30 ampere V = 0.52 volts Green reaction products. time = 1 hour i = 0.30 ampere V = 0.88 time = 3-1/2 hours Current had decreased to 0.05 ampere. Increased current i = 0.31 ampere V = 2.0 volts time = 4 hours i = 0.30 ampere V = 2.1 volts Gel surface covered with layer of reaction products. Surface mottled, 3 mils deep.	The film on the gel seems to be one of the major causes of the mottling and presumably is hindering th depth of cut. Replacing the gels periodically does not seem to improve cut or surface film.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-73 (con.) Run No. 2				Replaced gel and reservoir time = 0 i = 0.32 ampere V = 0.52 volts Green reaction products. time = 4 hours i = 0.31 ampere V = 0.52 volts Same gel and sample surface cut 6 mils deep.		
Run No. 3				Replaced gel and acid reservoir time = 0 i = 0.32 ampere V = 0.54 volts Green reaction products. time = 4 hours i = 0.32 ampere V = 2.35 volts Gel again covered with reaction products. Black insoluable flakes on sample. For all runs cathodes were 302 S.S. which acquired a copper colored film during run. At end of runs reservoir was green tinted.		
H-74	To electrolytically cut a 321 S.S. sample using the reservoir technique.	Same as H-71.	Same as H-72 using one run for extended period.	Gel area 2 sq inches thickness 1/4 inch. time = 0 i = 1.0 ampere V = 0.9 volts Green reaction products. time = 12.5 hours i = 0.74 ampere V = 3.35 volts Gel surface was covered with sludge. Areas void of the sludge produced the deepest cuts in the sample. Depth of cut was 10-11 mils with portion of surface not etched due to gel contour. Surface was very mottled and was reproduced in gel surface. A sample of the reservoir acid place in a beaker show that the etchant was gassing, the gassing continued for 36 hours.	The gassing of the etchant with reaction products is presumably the cause of the gel blistering noted in previous experiments. This gassing of the etchant seem to be a very detrimental factor in cutting flat plate with this system.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-75	Rerun H-74 using same 321 S.S. sample.	Same as H-73	Same as H-74	Gel area 2 sq inches thickness of 1/4 inch. Initial weight of sample 180.21 g time = 0 i = 0.54 ampere V = 0.93 volts Current dropped rapidly from 0.60 ampere to 0.20 ampere when voltage increased reproducing effect of experiment H-67, Run No. 2. Initially green reaction products were formed. time = 5 minutes i = 0.24 ampere V= 1.10 volts Brown reaction products. Voltage increased. time = 6 minutes i = 0.97 ampere V= 2.13 volts time = 5 hours i = 0.97 ampere V = 2.95 volts Final weight of sample 177.11 g. Bath was very dark green. Essentially same results as H-74. Bath liberated gas after experiment stopped. Depth of cut now 15-19 mils.	Reaction products and gassing still present. Gassing is probably due to a reaction between the HCl and HNO_3 acids when reaction products come into solutions.	Should investigate gel formulations without HNO_3 in order to eliminate gassing.
H-76	To prepare several HCl gels in effort to eliminate gas emission when reaction products have dissolved in etchant.	H-2220.1 36 g cellulose acetate (Type E-394-30) 120 cc 4 N HCl H-2220.2 24 g cellulose acetate (Type E-394-30) 120 cc 4 N HCl H-2220.3 24 g cellulose acetate (Type E-394-30) 120 cc 4 N HCl 1 ml Triton X-100 (surfactant)	Each sample mixed for 2 minutes in air blenderandcost in 800 ml beaker.	Within 30 minutes all mixtures had separated. H-2220.1 and H-2220.2 had separations near base of beaker. Both had separation between layers of acid. H-2220.3 separated only at top of mixture. Separation was above all cellulose acetate mixture. All three mixtures gelled firmly within 4 days and experienced normal syneresis. H-2220.3 was extremely smooth in texture and surface.	As a result of these observations a probable reason why separations occur might be air entrapment. Without a surfactant the acid is not able to displace any small air pockets in some of the cellulose acetate particles thus causing some to rise and others to sink. When a surfactant is added the etchant is able to displace the air entrapment producing a separation only at the top of the mixture.	Investigate etching characteristics of H-2220.3.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-77	Investigate etching characteristics of H-2220.3 prepared in H-76.	Same as H-2220.3 H-76	Place gel atop porous sand casting in petri dish. Add 4 N HCl acid reservoir with 1 ml of Triton X-100. Pickle 321 S.S. Sample 5 minutes in HCl and place over gel. Place a 302 S.S. cathode on either side of gel and apply potential.	Gel area approximately 2 sq inch. time = 0 i = 0.5 ampere V = 0.73 volts Surfactant caused foaming in bath. time = 2 hrs. i = 0.3 ampere V = 3.9 volts time = 14 hrs. i = 0.88 ampere V = 5.6 volts Foaming of reservoir so severe that foam came in contact with sample and etching is carried through foam. A very severe sludge had formed on sample surface. Only acid that would dissolve sludge was HF. Depth of etch was 25 mils at gel contact area and 20 mils where foam was in contact. Etchant was not gassing. When removed from reservoir.	Due to foaming a good indication of the etching characteristics of this gel could not be observed.	Repeat Expt. omitting Triton X-100 from bath.
H-78	Repeat H-77 except run for shorter period and omit Triton X-100 from bath.	Same as H-77	Same as H-77 except omit Triten X-100 from bath.	Initial weight sample 187.035 g time = 0 i = 0.5 ampere V = 0.73 volts time = 2-1/2 hrs. i = 0.24 ampere V = 3.3 volts Dark green products. Final sample weight 186.265 g. When sample remove products had diffused approximately 1/4 inch into the gel. Surface of gel was covered with black insoluable layer. This layer was slightly soluable in HF. Surface of sample was shiny with about 2 mils removed. No mottling even with sludge. Line definition of gel was quite good.	Again sludge on gel surface formed along with black insoluable layer. Etchant did not gas with dissolved reaction products.	Further study planned.

APPENDIX D (Continued)

Expt. No	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-79	Repeat H-78 using bath with HF.	Gel formulation: 24 g cellulose acetate (Type E-394-30) 120 cc 4 N HCl 1 ml Triton X-100 Bath formulation: 250 ml 4 N HCl 250 ml 30% HF solution.	Same as H-78 with bath corrections.	time = 0 Sample allowed to remain on gel without applied potential. time = 1 hr. apply voltage i = 0.31 ampere V = 0.58 volts Kept current essentially constant at 0.3 amperes. time = 2 hrs. i = 0.3 ampere V = 1.4 volts Depth of cut approximately 2 mils. Black film was still present on gel. No blistering of gel or gassing of etchant present.	HF did not seem to help the black film or sludge buildup when used in the reservoir.	Further study planned.
H-80	To etch a 302 S.S. sample using a new technique where etchant is forced over surface of gel.	24 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^- 0.5 ml Triton X-100	Cast gel in 100 ml beaker with section of glass tubing placed in beaker such that tubing will go through center of gel and be exposed at the surface. Produce flow over gel surface by connecting glass tubing to a reservoir raised above the gel surface. Place gel in container with sample atop and apply potential across. Etchant in reservoir is 3 N H and 1 M NO_3^-	Gel area 2.5 sq inch acid head was 8 inches. time = 0 i = 0.38 ampere V = 0.90 volts time = 30 minutes i = 0.44 ampere V = 0.96 volts Flow rate too great. Head reduced to 5 inches. New flow rate approximately 1 liter per hour. time = 90 minutes i = 0.40 ampere V = 0.97 volts Gel surface almost void of reaction products. Only dark ring around gel where firm contact made. Surface of sample was quite good. No indication present where tubing protruded from gel. A ridge around the etched surface where gel was in contact showed very little etch. Depth at other points was 2 mils.	Sample surface was quite good except where firm gel contact was present. The flow of etchant removed the reaction products fast enough to prevent a buildup at the anode surface.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-81	Repeat expt. H-80 with a few variations.	Same as H-80	Same as H-80.	Gel area 2.5 sq inches. Etchant head was 5 inches. time = 0 i = 0.60 ampere V = 0.96 volts Green reaction products. time = 2-1/2 hrs. i = 0.64 ampere V = 1.02 volts Flow rate again was approximately one liter per hour. Gel surface was similiar to H-79 except for a greater amount of reaction products at firm contact points. Depth of cut was again shallow at these contact points. Depth of cut was 4 mils. Surface of sample had slight indication where etchant flowed through glass tube.	Due to poor etch rate where gel was in contact with sample this system does not seem desirable. For prolonged cuts the area close to and above the acid feed tube would probably be etched at a different rate than the rest of the surface.	No further study planned.
H-82	To cut a 302 S. S. sample using a current density of 0.1 ampere per sq inch.	18 g cellulose acetate (Type E-394-30) 90 cc 3 N H^+ and 1 M NO_3^- 15 cc methanol 7.5 cc dibutyl phthalate.	Gel used four days after preparation. Place gel in petri dish with reservoir of 3 N H and 1 M NO_3^- acid. Allow sample to rest atop gel for approximately 1 hour prior to voltage application.	Gel area 4 sq inches Height 2 inches. time = 0 i = 0.4 ampere V = 0.80 volts time = 1 hr. i = 0.38 ampere V = 0.89 volts time = 19 hrs. i = 0.07 ampere V = 1.2 volts No sludge was present on gel surface. The reaction products had diffused 3/4 inch during the etching time. Depth of etch was 4 mils and surface finish was slightly mottled.	Results are quite good as compared to previous experiments. However, depth of cut was poor.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-83	Repeat H-82, but replace acid reservoir every three hours	Same as H-82	Same as H-82	Gel area 4 sq inches Height 2 inches time = 0 i = 0.4 ampere V = 0.77 volts Green products. time = 3 hrs. 15 min. i = 0.4 ampere V = 1.1 volts Change acid reservoir. Voltage was reduced to zero for approximently 30 seconds while reservoir was replaced. When voltage was applied again i = 0.4 ampere V = 2.1 volts A potential opposite to implied potential was noticed. Sample was removed. Etch depth was 3 mils. Surface finish was very good. Sample was replaced on gel. i = 0.4 ampere V = 2.25 volts. Large amount of liquid formed at anode surface now. time = 6 hrs. 25 min. i = 0.34 ampere V = 2.55 volts Depth now 5 mils. Surface discolored brownish. Acid reservoir replaced. i = 0.33 ampere V = 2.8 volts Surface of sample was again discolored. A large amount of liquid was present on gel surface. Diffusion through gel was nearly 3/4 inch. Depth of cut was now 6 mils. During experiment etchant was noticed to gas at sample surface and at gel surface. However, even with this gassing the gel surface was not deformed notecably.	Cutting rate decreases as the reaction products are formed and diffuse into gel. Mottling of the surface may occur only after experiment has been running for a considerable period of time.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-84	Repeat expt. H-83.	Same as H-83	Same as H-83 except do not reduce voltage to zero when reservoir replaced.	Gel area 4 sq inches. Height 2 inches. time = 0 i = 0.4 ampere V = 0.81 volts time = 3 hours i = 0.4 ampere V = 1.5 volts Replace reservoir, time = 4 hours i = 0.7 ampere V = 1.85 volts Low current, high voltage condition had existed for no more than 10 minutes. A reverse current produced by the gel when the implied voltage was reduced to zero was 0.17 ampere. Sample removed. Surface was shiny with 3 mils removed. Gel surface was void of liquid or sludge. Products had diffused approximently 1/2 inch. Etchant was gassing.	When the gel resistance builds up the sludge and excess liquid are formed at the sample surface. This results in poor etching rates and poor surface finishes.	Further study planned in effort to find etchant that will produce a minimum amount of deposites at the sample surface for a prolonged etch.
H-85	To examine the electrolytic etching characteristics cellulose acetate gels containing H_3PO_4.	32 g cellulose acetate (Type E-394-30) 27.6 ml HCl 8.4 ml HNO_3 4.0 ml H_3PO_4 120.0 ml H_2O 1 drop Triton X-100.	Place gel in usual acid reservoir and apply voltage in normal manner. Gel used 3 days following preparation. Allow 302 S.S. sample to rest on gel one hour prior to voltage application.	Gel area 1 sq inch. time = 0 i = 0.16 ampere V = 0.50 volts Dark green reaction products. time = 30 minutes i = 0.15 ampere V = 0.60 volts Products back diffused through gel 1/8 inch. time 5 hours i = 0.16 ampere V = 0.94 volts Products had diffused 1/2 inch. Liqueficution at anode quite small. No visible gassing observed at anode. Slice of gel near center showed diffusion of only 1/8 inch. Sample surface was good. Slightly mottled with depth nearly 5 mils.	Initial experiment indicates that these gels may improve etching characteristics.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretations of Results	Conclusions and Recommendations
H-86	To further investigate gel of expt. H-85.	Same as H-85	Same as H-85	Gel area 1 sq inch. time = 0 i = 0.16 ampere V = 1.75 volts High initial voltage of 6 volts accidentally applied caused high resistance of gel. Brown reaction products. time = 3 hours 25 minutes i = 0.15 ampere V = 1.97 volts Experiment stopped. Gel surface was good with little liquefaction at anode surface. Etch on sample was very uniform with 2 mils removed. Preliminary test to see if iron was being selectively removed gave no conclusive results.	The voltage across the gel seems to have a definite relation as to the valence state (color) of the products. Current densities of 0.15 a per sq inch seem to result in uniform surface finishes with little depth.	Investigate higher current densities.
H-87	To investigate phosphoric acid gels at higher current density.	Same as expt. H-85	Same as H-85 except initial voltage of 6 volts applied for 20 seconds.	Gel area 2 sq inches. time = 0 i = 0.5 ampere V = 2.2 volts Reaction products are yellow-brown. time = 30 minutes i = 0.5 ampere V = 2.5 volts time = 2 hours i = 0.41 ampere V = 2.8 volts Gel surface was unaffected by high current except for much greater liquid layer. Surface of sample was flat with depth of cut approximently 4 mils. Sample slipped on gel surface during run causing two images on sample.	Liquid at surface much greater for higher current densities.	Further study planned.

APPENDIX D (Continued)

Expt. No	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretations or Results	Conclusions and Recommendations
H-88	Repeat H-86	Same as H-85	Same as H-87	Gel area 2 sq inches. time = 0 i = 0.5 ampere V = 2.3 volts Yellow-brown products time = 2 hours i = 0.5 ampere V= 3.4 volts Slight sludge formed on gel surface. Sample was cut 10 mils to deepest areas and 4 mils at shallow areas. Surface of deep cut areas was mottled.	Higher current causes the formation of reaction products that interfere with the surface. Depth of cut was improved however.	Problem of build-up of reaction products at sample with high current densities again occurs.
H-89	To investigate etching characteristics of 3 N gel on PH15-7MO S.S. honeycomb core. 1-1/2 mil wall thickness	36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-.	Gel used 10 days after preparation. Place honeycomb sample in apparatus used in previous honeycomb cuts. Use 500 g weight atop honeycomb. Apply potential across gel.	Honeycomb area 4 sq inch. time = 0 i = 0.76 ampere V = 3.2 volts Brown reaction products. time = 25 minutes i = 0.87 ampere V = 3.05 volts When sample removed a large amount of liquid had formed around periphery of contact area. Honeycomb sample was very flat with slight projections corresponding to excess acid regions. Depth of cut was 15 mils	Results show that PH15-7Mo S.S. honeycomb can be cut using the 3 N gel system.	Further study planned.

APPENDIX D (Continued)

Expt. No	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretations of Results	Conclusions and Recommendations
H-90	Investigate electrolytic etching characteristics of 3 N gels on 305 S.S. honeycomb core. Wall thickness is 4 mils.	Same as H-89	Same as H-89 except gel 14 days old.	Honeycomb area 4 sq inches time = 0 i = 0.65 ampere V = 3.0 volts Brown reaction products. time = 40 minutes i = 0.82 ampere V = 2.9 volts Gel surface similiar to H-89. The honeycomb finish was scalloped with high spots at the welded junctions. Depth of cut to nodes was 15 mils. Estimated 5 mils difference in height of nodes and lower parts. The liquid on the gel surface formed during the cut had "climbed" the total height of the honeycomb (3/4 inch) in the crevice at the welded junction.	Although the surface of the honeycomb was scalloped the results indicate that flat cuts of 305 S.S. core are possible. The "climbing" effect of the reaction products may become a problem	Concentrate on cutting PH15-7Mo S.S. honeycomb in the immediate future.
H-91	To cut a PH 15-7Mo S.S. honeycomb for an extended period to determine the problems that may arise in attempting deep cuts.	36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-.	Gel prepared 10 days prior to use. Place honeycomb in apparatus and allow honeycomb to "walk in". Apply potential across gel in usual manner.	Honeycomb area 16 sq inches time = 0 i = 1.5 ampere V = 3.2 volts Reaction products are brown. time = 3 hours i = 1.7 ampere V = 3.1 volts Large amount of liquid was present around perimeter of gel. Gel was warped noticably. The honeycomb core was cut in a convex manner. Depth of cut at center was 50 mils and was 100 mils around perimeter. Anodic and cathodic areas were present at welded junctions. Finish in center of honeycomb sample was flat.	Liquid around edge of honeycomb area was due to the warping of gel.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretations of Results	Conclusions and Recommendations
H-92	To repeat H-90 drying off gel every 30 minutes.	Same as H-91.	Same as H-91 except dry off gel every 30 minutes.	Honeycomb area 16 sq inches. time = 0 i = 1.75 ampere V = 3.5 volts Brown reaction products. time = 35 minutes Raise honeycomb and dry off gel. Liquid formation uniform over gel surface. Continue = i = 1.85 ampere V = 3.4 volts time = 60 minutes. Dry off gel. Liquid more prominent around perimeter of gel, indicating warping. Continue = i = 2.00 ampere V = 3.3 volts time = 1 hour 40 minutes dry off gel. Liquid on gel surface very prominent around gel perimeter and very slight in center of gel. Continue = i = 2.00 ampere V = 3.3 volts time = 2 hours 35 minutes i = 2.00 ampere V = 3.35 volts Experiment stopped. Gel surface was almost dry as center indicating negligible etch taking place. Around gel perimeter liquid layer was very heavy. Warping of gel was easily observed. Honeycomb surface was very flat in center becoming scalloped toward edges. Depth of cut in center area was 50 mils and 70 mils around edge.	Results indicate that warping occurs after 60 minutes and becomes so severe that contours and dimensional control cannot be held.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-93	To try new method of cutting honeycomb core.	36 g cellulose acetate (Type E-394-30) 120 cc 3 N H^+ and 1 M NO_3^-.	Gel prepared 12 days prior to use. Place PH15-7 Mo honeycomb sample on flat plate with gel on top of honeycomb. Place another honeycomb sample atop gel as cathode. Allow gel to "walk-in" honeycomb.	Honeycomb area 16 sq inches time = 0 i = 1.9 ampere V = 3.2 volts Brown reaction products. Liquid formed on gel surface now flowed down honeycomb sides. time = 90 minutes i = 2.1 ampere V = 3.2 volts Run stopped due to warping of gel. Honeycomb was very flat with cut of 40 to 55 mils. No visible indications of etching by liquid running down sides of honeycomb. Litmus paper indicated very acid when in contact with this liquid.	This method of cutting has the advantage of allowing the reaction products to flow away from the cutting area and thus eliminating the necessity of their diffusion. The liquid running down the sides of the honeycomb may be detrimental in long cutting times.	Further study planned.
H-94	Cut a 9 inch by 9 inch section of PH15-7 Mo honeycomb core.	Same as H-93.	Same as H-93. Gel thickness was 3/4 inch.	Honeycomb area 81 sq inches. time = 0 i = 5.8 ampere V = 3.0 volts Brown reaction products. time = 1 hour i = 5.65 ampere V = 3.2 volts Experiment stopped due to gel warping. Surface finish of honeycomb was very flat but depth of etch was uneven. Depth varied from 10 to 30 mils.	Significant results of this experiment was the case in which the large gel could be handled prior to use. Gel was rigid and firm enough to permit unsupported handling. Gel warping was again problem.	Further investigations to reduce warping.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
H-95	To etch a PH15-7Mo honeycomb sample submerged in kerosene bath. The kerosene bath is an attempt to reduce gel warping.	36 g cellulose acetate (Type E-493-30) 120 cc 3 N H^+ and 1 M NO_3^-.	Place honeycomb sample on flat plate in large container with gel atop. Place honeycomb cathode over gel with 400 g weight on cathode. Fill container with kerosene until surface is approximately half-way up cathode walls. Apply potential across gel.	Gel area 16 sq inches. time = 0 i = 1.5 ampere V = 3.2 volts Reaction products were brown and streamed down honeycomb walls. time = 30 minutes i = 1.65 ampere V = 2.95 volts No visible warping of gel. time = 60 minutes i = 1.70 ampere V = 2.90 volts Still no sing of warping. time = 90 minutes i = 1.65 ampere V = 2.90 volts No observable warping. Reaction products collecting at flat base plate. time = 120 minutes i = 1.60 ampere V = 3.00 volts Experiment stopped. No visible gel warping. Kerosene bath was warm, approximately 80°F. Gel had no visible effects of being submerged in kerosene. Honeycomb sample was very flat. Depth of cut was 50 mils.	Kerosene bath has advantages of removing liquid products rapidly, cooling gel, eliminating acid fumes from honeycomb, and eliminating warping. Even greater depths and cutting times with corresponding good surface finishes appear very feasible.	Further study planned.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-28	Reinforce a gel etchant prepared from a suspension of cellulose acetate in acid solution by adding and coagulating a fluorocarbon in the gel mixture.	L-1750 24.0 g cellulose acetate type E 394-30 19.0 cc 38° Be HNO_3 24.0 cc 20° Be HCl 77.0 cc H_2O 30.0 cc fluorocarbon latex L-242	Mix formulation for 60 seconds on Waring Blender PM-5A. Cast gel in a ceramic teacup. Set gel in a petri dish apex up. Add an acid reservoir solution to the petri dish, 4 M hydrochloric and 2 M nitric acid. Place a 321 S.S. plate on the gel apex and observe etch characteristics.	The gel appeared firmer but more porous than gel formulation without coagulated fluorocarbon latex. Diffusion rates did not appear altered by the addition of fluorocarbon latex to the standard cellulose acetate gels. This gel deteriorated at temperatures past 140° F which is no significant improvement in temperature resistance.		Augmenting gels containing cellulose acetate suspended in acid solutions with fluorocarbon latex slightly improves the strength of the gel, creates porosity, and only slightly improves the temperature resistance.
L-29	Investigate a gel etchant containing carboxymethyl cellulose, ammonium bifluoride and nitric acid solution for etching titanium.	L-1752.1 18.0 g carboxymethyl cellulose type 7 HP 20.0 cc CH_3OH 13.7 g $NH_4F \cdot HF$ 19.3 g 38° Be HNO_3 90.0 cc H_2O	Hand mix formulations in a plastic beaker and cast into a plastic lined petri dish. Cut a 1-inch square sample from each gel and place a 6Al-4v titanium alloy coupon on gel sample. Observe etch characteristics.	L-1752.1 solution gelled almost immediately into a firm gel. A brownish discoloration at the gel to metal interface immediately. Several minutes later the gel near the interface turned opaque and the etching stopped. A caulky, white deposit developed at the interface stopping the etch reaction.		A gel etchant can be prepared using ammonium bifluoride nitric acid and carboxymethyl cellulose. During etching a white, caulky deposit builds up at the gel to metal interface restricting the etch reaction.
		L-1752.2 12.0 g carboxymethyl cellulose type 7HP 20.0 cc CH_3OH 13.7 g $NH_4F \cdot HF$ 19.3 cc 38° Be HNO_3 90.0 cc H_2O		L-1752.2 - This solution did not gel to a firm solid.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-30	To investigate the effect of applying a low voltage to a carboxymethyl cellulose plus hydrochloric acid gel between two S.S. plate electrodes.	L-1756 12.0 g carboxymethyl cellulose type 7 HP 20.0 cc CH_3OH 36.0 cc 20° Be HCl 84.0 cc H_2O	Hand mix formulation and cast into a petri dish. Cut a 3/4 x 3/4 sq in. by 1/4 inch thick sample. Position the gel section between two S.S. electrodes so that the current will travel 1/4 inch through the gel. Connect an ammeter, variable resistance, and a 6 v direct current source in series with the cell and and a voltmeter in parallel to the cell. Adjust the rheostat to give a small current density and a low voltage potential across the cell. Record time, amperes, volts and observations.	Application of 0.8 to 3.0 v across the cell resulted in a current density of approximately 0.9 a/sq in. A free gel 1/4 inch thick slowly increased in resistance from 3 ohms to 6.5 ohms in 15 minutes. The gel could be regenerated to its original resistance by soaking the used gel in hydrochloric acid. However, the regenerated, lower resistance was of short duration when the current was reapplied. No deposit other than hydrogen gas can be seen on the cathode when the applied voltages are less than 3 v. When voltages past 3 v are applied a black deposit develops at the cathode. This deposit dissolves in hydrochloric acid.	In previous experiments the driving forces were reduction in free energies, which takes place when free metal changes to metal ion, and concentration gradients causing ion diffusion. An applied potential appears to increase the etch rate by adding extra electrode potential and increasing ion diffusion through ion attraction to oppositely charged electrodes.	Application of a direct current voltage across a thin section of gel containing hydrochloric acid electrolyte removes approximately 3 mils from a S.S. plate anode per hour when the current density is 0.9 a per sq in. There is a steady rise in resistance across the cell with time, which probably results from depletion of hydrogen ion and dehydration of the gel. Metal ion deposits at the cathode when the applied voltage across the cell exceeds 3 v. Recommend future experiments where hydrogen ion and water can regenerate the gel cell.

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-31	To investigate the possibility of oxidizing and removing metal from an anode plate, diffusing the metal ion through a gel electrolyte and depositing the metal ion on a cathode plate.	L-1764.1 27.0 g carboxymethyl cellulose type 7 HP 20.0 cc CH_3OH 9.4 g $Fe(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$ 12.0 cc 98% H_2SO_4 108.0 cc H_2O L-1764.2 36.0 g carboxymethyl cellulose type 7 HP 20.0 cc CH_3OH 9.4 g $Fe(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$ 12.0 cc 98% H_2SO_4 108.0 cc H_2O	Hand mix formulations in a beaker and cast into petri dishes. From each gel cut a section 0.25 sq in. by 1/4 in. thick and place gel sections between S.S. plate electrodes so that the current will travel 1/4 in. through the gel. Connect an ammeter, variable resistance, and a 6 v direct current source in series with each cell. Adjust the rheostat to give a small current density and a low voltage potential across each cell. Record time, amperes, volts and observations	Formulation A: The initial current across the cell was 0.33 a with a voltage of 3.5 v across the cell. The resistance steadily increased with time. 24 minutes after start of current the current dropped to 0.07 a with a voltage of 6.2 v across the cell. Gassing was noticed at the cathode initially. The cathode plate developed a heavy black deposit that dissolved in hydrochloric acid approximately a half mil removal was noticed on the anode surface. The final gel was slightly dehydrated, hard and brittle after passing current for several minutes. Formulation B: The same steady increase in cell resistance and dark cathode deposits were noticed.	The initial low resistance across the cell probably was the result of a low potential drop at the cathode resulting from the low potential required to reduce hydrogen ion. As the hydrogen ion depleted the potential drop at the cathode increased until a potential difference reached the deposition voltage of the metal ions removed from the anode. Also the increase in resistance was substantiated by dehydration of the gel electrolyte resulting from high voltage inefficiency.	A steady state condition where a relatively stable potential drop and current density would be attained across this particular gel electrolyte was not observed. Future experiments are required to determine exact voltage (or energy) requirements to simultaneously remove metal at the cathode. Low voltages and current inefficiencies will be required in order to prevent dehydration of the gel electrolyte.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-32	To investigate the possibility of oxidizing and removing metal from an anode plate, diffusing the metal ion through a gel electrolyte and depositing the metal ion on a cathode plate.	L-1769 36.0 g cellulose acetate type E-394-30 19.0 cc 38° Be HNO_3 48.0 cc 20° Be HCl 53.0 cc H_2O	Mix formulation for 60 seconds on Waring Blender PM-5A. Cast gel into a petri dish. Cut a section of gel 0.375 sq in. by 1/4 in. thick and place gel section between two S.S. plate electrodes so that the current will travel 1/4 in. through the gel. Connect 6 v direct current source, ammeter, voltmeter and rheostat in same manner as Expt. L-31. Record time, amperes, volts and observations.	The initial current across the cell was 0.45 a with a voltage of 1.2 v across the cell. The resistance steadily increased with time. 27 minutes after start of current, the current dropped to 0.27 a with a voltage of 3.6 v across the cell. When the voltage drop across the cell exceeded 3.6 v, gassing stopped at the cathode. Approximately 1/2 mil was removed from the anode. The etched surface on the anode was bright and free from deposit. The gel electrolyte was very dark from metal ion concentration. The gel surface adjacent to the cathode plate appears to be dehydrated and caked. The gel surface adjacent to the anode plate is moist. The outline of the gel has been exactly reproduced on the anode plate. There is a dark deposit on the cathode surface which dissolves in hydrochloric acid.	The steady increase in potential difference across the cell and decreased current density probably results from hydrogen ion depletion and gel dehydration as explained in Expt. L-31.	A gel electrolyte containing hydrochloric acid, nitric acid, and cellulose acetate initially has a low potential drop (1.2 v) and a high current density (1.2 a/sq in.) across the gel cell. As time progresses the resistance increases, voltage drop increases and current decreases to a negligible amount. The ion combination in this experiment is more favorable than that used in Expt. L-31. Future experiments should provide means of replenishing hydrogen ion at the cathode.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-33	To replenish the acid electrolyte to a gel cell by submerging the cathode and part of the gel in an acid reservoir.	L-1772 24.0 g cellulose acetate type E-394-30 9.6 cc 38° Be HNO_3 24.0 cc 20° Be HCl 86.4 cc H_2O	Mix formulation for 60 seconds in Waring Blender. Cast gel into petri dish. Cut a section of gel 0.75 sq in. by 3/4 in. thick. Pickle a 321 S.S. plate and strap gel section to the plate in petri dish with plate upward and connect to anode terminal of direct current source. Fill the petri dish with acid solution 2 M nitric and 4 M hydrochloric acid until the solution level is 1/4 in. from the plate. Hook a strap of stainless steel over the edge of the petri dish into the acid solution as a cathode. Connect the cell in series with a 6 v direct current source, ammeter and rheostat. Connect the probes of a vacuum tube voltmeter in parallel to the cell. Record time, amperes, volts, ohms and observations.	The initial potential drop across the cell was 1.10 v with a current density of 0.60 a per sq in. The cathode strap is gassing profusely and no gassing can be observed at the anode plate. In 79 minutes the current density dropped to 0.47 a per sq in. with a corresponding potential drop across the cell of 2.4 v. The etched anode is bright and smooth with no signs of insoluble residue at the interface. Approximately 2 mils were removed with good line definition. There appears to be more diffusion through the center of the gel than at the edges.	The success of this experiment can be attributed to the relatively low current resistance of these gel systems to current densities used in this experiment and to the low junction potential drops at the acid reservoir to gel interface, and the gel to solution film at the gel to metal plate interface. The major contributors to the carrying of current through the gel electrolyte are the mobile chloride ions in the direction of the anode plate and the highly mobile hydrogen ions in the direction of the cathode. To a lesser extent, the metal ions from anodic solution contribute to the current. The exact percentage of current carried by each ionic specie (transference) should be determined.	The technique of immersing part of the gel and the cathode of a gel cell in an acid bath appears successful with only a slight increase in voltage drop and decrease in current for a period exceeding 1 hour. There appears to be sufficient diffusion of metal ion and acid ion through the gel so that a semisteady state can be obtained. This technique will be thoroughly investigated in future experiments for longer lengths of time.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-34	Continued investigation of replenishing the acid electrolyte to a gel cell by submerging the cathode and part of the gel in an acid reservoir.	L-3003 24.0 g cellulose acetate type E-394-30 9.6 cc 38° Be HNO_3 24.0 cc 20° Be HCl 86.4 cc H_2O	Mix formulation for 60 seconds in Waring Blender. Cast gel into a juice glass with a 1.5 in. inner diameter. Remove the gel from the cup mold and cut the gel to a height of 3/4 in. from the image of the bottom of the glass. Pickle a 321 S.S. plate and strap the gel to the plate with mylar tape. Place in petri dish with plate up. Fill the petri dish with acid solution which is 1 M nitric and 2 M hydrochloric acid until the solution level is 1/4 in. from the gel to plate interface. Immerse a S.S. cathode cathode into the acid bath and connect the cell in series with a 6 v rectifier, a 12-ohm rheostat, and an ammeter. Connect the probes of a vacuum tube voltmeter in parallel to the cell.	The initial potential drop across the cell was 0.80 v with a current density of 0.27 a per sq in. After 102 minutes, the potential drop across the cell increased to 2.3 v and current density decreased to 0.21 a per sq in. A steady current of 0.27 a per sq in. existed for over 1 hour. There was profuse gassing at the cathode and no noticeable gassing at the anode. The dark metal ion migrated through the gel to the solution level of the acid reservoir. The final gel condition was poor and cracked in a couple places. The etched surface on the anode was uneven because of the gel cracking. No sludge deposit can be seen at the gel to anode plate interface. Approximately 3-4 mils were removed from the plate.		A steady state condition existed for a period exceeding 1 hour where the current density was 0.26 a per sq in. and the potential drop across the cell remained at 0.8 to 1.0 v. Reason for gel breakdown will be determined.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-35	Continued investigation of replenishing the acid electrolyte to a gel cell by submerging the cathode and part of the gel in an acid reservoir.	L-3006 24.0 g cellulose acetate type E-394-30 9.6 cc 38° Be HNO_3 24.0 cc 20° Be HCl 86.4 cc H_2O	Same as Expt. L-34. Continue etching the same etched S.S. surface electrolytically etched in Expt. L-34.	The initial potential drop across the cell was 0.85 v with a current density of 0.27 a per sq in. This current density and potential drop remained steady for over 1 hour and then the current density decreased to 0.21 a per sq in. with 2.3 v across the cell. The cell maintained this second steady state condition for over 100 minutes. The gel did not crack or deteriorate. Can see small irregularities on the plate surface which are duplications from irregularities in the cast gel surface. Line definition is good. The etch surface is smooth with approximately 4-5 mils removed.	A change in the gel structure resulting from metal ion absorption may be responsible for the change in the current density and potential drop after approximately 60 minutes of electrolytic etching.	An initial high current, low voltage steady state condition existed for the first 60 minutes and changed to a second steady state condition having lower current density and higher potential drop for the duration of the experiment. This is the same phenomenon noticed in Expt. L-34.
L-36	Continued investigation of replenishing the acid electrolyte to a gell cell by submerging the cathode and part of the gel in an acid reservoir.	L-3009 24.0 g cellulose acetate type E-394-30 9.6 cc 38° Be HNO_3 24.0 cc 20° Be HCl 86.4 cc H_2O	Same as Expt. L-34 except allow plate to etch 60 minutes before applying current to cell. Extend reaction time for over 8 hours. Continue etching the same etched S.S. surface electrolytically etched in Expts. L-35 and L-34.	A lower initial current density of 0.22 a per sq in. and a higher initial voltage drop of 1.8 v was observed across the cell where the gel was permitted to etch for 60 minutes prior to current applications. A steady current density of 0.20 a per sq in. with a corresponding voltage drop of 2.1 to 2.5 v was observed for almost 8 hours. The gel surface became slightly deteriorated from nitrate ion gassing to nitrous oxide in the gel voids. The gel and acid both are dark from metal migration. Etch surface is only slightly irregular from small irregularities in the in the gel. Approximately 12 to 14 mils were removed with this single gel in 12-1/2 hours.		A gel cell, containing a submerged cathode and a gel partially submerged in a reservoir of acid solution, will maintain a steady current of 0.20 a per sq in. and a voltage across the cell of 2.1 to 2.5 v over a time interval of 12-1/2 hours. Etch rate is a little over 1 mil per hour with a relatively smooth surface and a good line definition. Future experiments will determine if higher current densities can be used to increase the etch rate.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-37	Continued investigation of replenishing the acid electrolyte to a gel cell by submerging the the cathode and part of the gel in an acid reservoir.	L-3014 24.0 g cellulose acetate type E-394-30 9.6 cc 38^{o} Be HNO_3 24.0 cc 20^{o} Be HCl 86.4 cc H_2O	Same as Expt. L-34. Continue etching the same etched S.S. surface electrolytically etched in Expts. L-36, L-35 and L-34.	After 120 minutes the current density decreased to 0.18 a per sq in. and the potential drop across the cell increased to 3.2 v. The current and voltage remained at these values for over 3 hours. The gel is in fair condition. The plate surface is even and bright. The gel shrinkage was 2.1 percent during the electrolytic action for over 3 hours. The average accumulated metal removal over the 1.76 sq in. of etched surface for Expts. L-34 through L-37 was 23 mils. The center was less deep than the edges because of the contour of the gel mold.	A current efficiency estimation was calculated using datum from Expts. L-34 through L-37. The stainless steel metal was assumed to be oxidized at the anode to divalent ferrous ion, divalent nickelous ion, and trivalent chronic ion. This assumption is substantiated with free energy data and kinetic considerations. The total gram equivalents of metal removed calculated to 0.232 g equivalents, which multiplied times Faraday's constant gives 22,360 coulombs of electricity to oxidize 5.88 g of stainless steel. The total ampere-hours added up to 8,236, which said 29,650 coulombs of electricity passed through the cell. The ratio of these two coulomb values gives a 75% current efficiency which is probably within 10% error.	An etch rate in the neighborhood of 1 mil per hour can be maintained with a steady current density for several hours with a current efficiency of around 75 percent.
L-38	To prepare a gel electrolyte which has potassium dichromate oxidant substituted for nitrate oxidant.	L-3020 24.0 g cellulose acetate type E-394-30 17.6 g $K_2Cr_2O_7$ 18.0 cc 20^{o} Be HCl 100.0 cc H_2O	Mix formulation for 1 minute in a Waring Blender and cast into a plastic juice glass. Prepare a gel cell in the same manner as Expt. L-34 only use an acid bath, 0.5 M $K_2Cr_2O_7$ and 1.5 M HCl.	This formulation remained fluid and did not gel.	The author theorizes that the slight deterioration of gels in previous experiments results from nitrate reduction to nitrous oxide during oxidation of ferrous to ferric ion. This reaction takes place in the gel and fills the small gel voids and eventually cracks the closed cells because of gas pressure buildup. If a now gassing oxidant can be used this problem will be eliminated.	The presence of potassium dichromate salts prevents gelation of suspensions of cellulose acetate in weak acid solutions.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-39	Determine if the gel shrinkage during applied potential etching is the result of interaction between metallic actions and the cellulose chains as the result of continued acid hydrolysis of the cellulose acetate and continued syneresis.	L-3023 24.0 g cellulose acetate type E-394-30 9.6 cc 38° Be HNO_3 24.0 cc 20° Be HCl 86.4 cc H_2O	Prepare gel cell in the same manner as Expt. L-34 only permit gel to age for 14 days before assembly of cell. Cut a gel section 1-9/16 x 1-9/16 sq in.	Applied a current to the gel cell for 7-1/2 hours. The gel surface is in fair condition. If there was gel shrinkage it could not be measured. Line definition around the edge of the etched surface is relatively sharp compared to previous experiments. The edges have a few places where differential etching has taken place.	In a short time after initial solidification, a gel will undergo its major shrinkage and then remain relatively constant and its dimensions. The intent of this experiment is to prepare a cell after the gel dimension has stabilized.	Permitting a cellulose acetate gel to stand for 14 days before assembly into a cell, results in a negligible shrinkage during etching. The shrinkage noticed in previous experiments probably are the results of further acid hydrolysis of the cellulose acetate and dehydration of the gel.
L-40	Determine the effectiveness of a gel cell when the etch surface is doubled.	L-3026 24.0 g cellulose acetate type E-394-30 9.6 cc 38° Be HNO_3 24.0 cc 20° Be 86.4 cc H_2O	Prepare a gel in the same manner as Expt. L-34 except cut a gel section 5.0 sq in. from the same aged gel cast into a petri dish and used in Expt. L-39.	The current density remained at 0.086 a per sq in. with a corresponding potential drop of 1.2 to 1.5 v for over 8 hours to the end of the experiment. Gel appeared in fair condition. The etched surface was slightly rough but uniform in depth of metal removal except for two small channel areas at the edge of the etch area. Line definition is excellent. Etch depth is approximately 6 mils.		Larger gel to plate surface areas resulted in an improved steady state current and voltage. The increase in etch area and lowering of the current density resulted in a decreased resistance across the cell and a corresponding lower potential drop.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-41	Prepare a cellulose acetate gel with a solution low in acid concentration and assemble into a cell having a reservoir of weak acid.	L-3028 24.0 g cellulose acetate type E-394-30 12.0 cc 20° Be HCl 4.8 cc 38° Be HNO_3 103.2 cc H_2O	Mix formulation for 60 seconds in a Waring Blender and cast into a plastic juice glass. Prepare a gel cell in the same manner as Expt. L-34 except use an acid reservoir solution which is 1 M HCl and 0.5 M HNO_3.	The initial current density was 0.19 a per sq in. with a corresponding potential drop of 2.5 v across the cell. This current density and potential drop remained constant for 2 hours, at which time the experiment was stopped. The color of the metal ion at the gel interface was reddish brown rather than the usual muddy green. Gel is in perfect condition. There appeared to be a smaller meniscus around the periphery of the gel than usual. Etched surface is smooth.	It appears that the current density and potential drop are independent of acid concentrations at the steady state values observed in these experiments. However, current density can be increased and potential drop decreased for a short initial duration by increasing the acid concentration. This phenomenon hints that another variable such as metal ion diffusion at the anode surface is rate controlling.	Gels in previous experiments, having a gel with higher acid content, had an initial high current density and a low potential drop. After 60 minutes there was a change to a steady, lower current density of 0.19 a per sq in. and a higher potential drop of 2.1 to 2.5 v. This cell with a gel of low acid content and reservoir of low acid content started immediately at 0.19 a per sq in. with a corresponding 2.5 v potential drop.
L-42	Prepare a cell containing a cellulose acetate gel and an acid reservoir having only hydrochloric acid electrolyte.	L-3031 24.0 g cellulose acetate type E-394-30 36.0 cc 20° Be HCl 84.0 cc H_2O	Mix formulation for 60 seconds in Waring Blender. Cast in a 1.5 in. diameter juice glass. Prepare a cell in the same manner as Expt. L-34 except use an acid reservoir solution which is 3 M HCl.	The initial current density was 0.24 a per sq in. with a corresponding potential drop of 1.2 v. The current density steadily decreased to 0.16 a per sq in. and the potential drop across the cell increased to 3.0 v after 2-hours operation. A viscous-like solution formed a larger than usual meniscus around the periphery of the gel. A gel-like sludge solution developed at the gel to plate interface. This sludge was easily washed from the gel. The gel is in perfect condition. The metal migration colored the gel a clear forest green compared to a dark muddy green in previous experiments containing nitrate ion. The etched surface on the plate is extremely smooth but slightly pitted.	The release of free energy plus the applied electrode voltage, appears to be sufficient potential energy to overcome irreversibilities when stainless steel is oxidized to metal ions at the anode surface. This takes place without help from nitrate ion oxidation potential. However the nitrate ion appears to alter the anode products to a more soluble and more diffusible ion state in previous experiments.	The elimination of nitrate ion from the gel and the cell reservoir resulted in reaction products which differed considerably in color and diffusibility through the gel. The reaction products form a viscous sludge solution at the gel to metal interface which appears to cause a steady increase in cell resistance. The gel remains in perfect shape and the etched surface is extremely smooth except for a few small surface pits.

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-43	Investigate a cell containing a gel prepared from carboxymethyl cellulose.	L-3034 15.0 g carboxymethyl cellulose type 7HP 20.0 cc CH_3OH 9.6 cc 38° Be HNO_3 24.0 cc 20° Be HCl	Hand mix formulation and cast into a 1.5 in. diameter juice glass. Prepare a cell in the same manner as Expt. L-34 except substitute 15.0 g carboxymethyl cellulose plus 20.0 cc CH_3OH for the 24.0 g cellulose acetate in the gel formulation. Use the same acid strengths used in Expt. L-34 for gel formulation and acid reservoir.	The initial current density was 0.21 a per sq in. with a corresponding potential drop of 2.1 v. These values remained constant for almost 2 hours at which time the experiment was stopped. The gel developed a crust at the gel to metal interface and is shrinking appreciably where the metal ion is concentrated. Etched surface on plate is relatively smooth.		A cell prepared with a gel having carboxymethyl cellulose substituted for the cellulose acetate does not appreciably alter the initial current density and potential drop across a cell. The gel formed a hard crust at the gel to plate interface and had a tendency to shrink where the metal ions were concentrated.
L-44	To investigate three new gel formulations and run their respective gel cells in series using the same current source.	L-3037.1 - Gel 1 15.0 g carboxymethyl cellulose type 7HP 20.0 cc CH_3OH 9.6 cc 38° Be HNO_3 24.0 cc 20° Be HCl 86.4 cc H_2O L-3037.2 - Gel 2 24.0 g cellulose acetate type E-394-30 60.0 cc CH_3OH 24.0 cc 20° Be HCl 9.6 cc 38° Be HNO_3 26.4 cc H_2O	Mix formulations and cast into a 1.5 in. diameter juice glass. Prepare a cell from each gel sample per Expt. L-34. Connect the three cells in series and in series with a 12-ohm rheostat, ammeter and a 6 v rectifier. Add an acid reservoir 2 $\underline{M}$ HCl and and 1 $\underline{M}$ HNO_3 to cells containing Gels 1 and 2. Add an acid 0.66 $\underline{M}$ HNO_3 and 1.33 $\underline{M}$ HCl to cells containing Gel 3. Run the three cells simultaneously from the same 6 v direct current source.	Cell prepared with Gel 1: The voltage drop across the cell increased from 1.0 v to 2.2 v and the current density decreased from 0.14 to 0.045 a per sq in. after 2 hours continuous etching. The gel shrank 12% at the interface. A 1/16 in. thick crust saturated with metal ion developed at the interface. Etchant surface is uneven but bright. Cell prepared with Gel 2: The voltage drop across the cell increased from 0.8 to 2.8 v and the current density decreased from 0.14 to 0.045 a per sq in. after 2 hours continuous etching. The gel shrank 4.3% at the interface. Gel appears in perfect shape with no signs of deterioration. Etched surface is bright and smooth.		Running cells in direct current series is not a good experimental procedure because a large increase in resistance in one cell will result in a decrease in current in the other cells thereby introducing an extraneous parameter. A cell having a gel prepared from carboxymethyl cellulose increases in resistance with time because of the development of a low conductive crust high in metal concentration, in the gel region adjacent to the etched surface.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-44 (con.)		L-3037.3 - Gel 3 24.0 g cellulose acetate type E-394-30 16.1 cc 20° Be HCl 6.4 cc 38° Be HNO_3 97.5 cc H_2O		Cell prepared with Gel 3: The voltage drop remained essentially constant and the current density decreased from 0.14 to 0.045 a per sq in. after 2 hours continuous etching. The gel showed no signs of deterioration. The metal ion in the gel adjacent to the interface is yellow brown and muddy green through the remainder of the gel. The etched surface is even but rough.		A cell having a gel prepared from cellulose acetate and a 50/50 mixture of methyl alcohol and acid solution increases in resistance with time. The etched surface is very smooth. A cell having a gel prepared from cellulose acetate and a weak acid solution only has the least increase in resistance with time. The etched surface is even but rough in finish.
L-45	To investigate a cell containing a gel prepared from cellulose acetate, methyl alcohol, and a small amount of weak hydrochloric acid.	L-3042.1 24.0 g cellulose acetate type E-394-30 90.0 cc CH_3OH 9.0 cc 20° Be HCl 21.0 cc H_2O	Mix formulation in Waring Blender and cast into a 1.5 in. diameter juice glass. Prepare a cell in the same manner as Expt. L-34 except use an acid solution reservoir which is 3 <u>M</u> hydrochloric acid.	The initial current density was 0.20 a per sq in. with a corresponding potential drop of 7.1 v. The high potential drop caused heating in the region of the gel to plate interface. The potential drop across the cell was reduced by increasing the rheostat resistance. The current density dropped to 0.11 a per sq in. with a corresponding potential drop of 5.0 v. The cell remained steady with these values for 3 hours. A gel-like crust high in metal ion concentration developed at the gel to plate interface. Gel is in perfect shape with no deterioration. The metal ion in the gel is clear forest green. The etched surface is very bright and smooth.		The elimination of nitric acid and substitution of a large percentage of the water solvent with methyl alcohol resulted in a gel cell having high resistance, different diffusion properties and metal ion products different in color. The gel appeared to have improved resistance to deterioration and etched an extremely bright and smooth surface. The largest drawback was the development of a gel-like sludge at the gel to plate interface, which probably contributed to the high cell resistance.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-46	Continued investigation of a cell containing a gel prepared from cellulose acetate, methyl alcohol, and a small amount of weak hydrochloric acid.	L-3046.1 24.0 g cellulose acetate type E-394-30 60.0 cc CH_3OH 6.0 cc 20° Be HCl 54.0 cc H_2O	Same as Expt. L-45.	The gel showed little signs of shrinkage in the mold and was more fragile than previous gels. The gel was broken into two halves during removal from the molds. Positioned the two halves together in the cell. The initial current density was 0.21 a per sq in. with a corresponding potential drop of 1.7 v across the cell. Two hours later the density decreased to 0.18 a per sq in. with a corresponding potential drop of 2.3 v and remained at this value for almost 14 hours until the end of the experiment. The gel deteriorated during etching. The etched surface is uneven from gel deterioration. However the surface finish is smooth and bright.		A gel prepared with methyl alcohol and low hydrochloric acid concentration shows a remarkable reduction in shrinkage, good ion diffusion, and low resistance. However the gel is fragile and deteriorates much easier than previous experiments.
L-47	To investigate a cell containing a gel prepared from cellulose acetate, methyl alcohol, hydrochloric acid and dibutyl phthalate.	L-3049 24.0 g cellulose acetate type E-394-30 60.0 cc CH_3OH 36.0 cc 20° Be HCl 24.0 cc H_2O 20.0 cc dibutyl phthalate	Prepare gel and cell in the same manner as Expt. L-45.	The initial current density was 0.28 a per sq in. with a corresponding potential drop of 1.8 v across the cell. One and a half hours later the current density steadily decreased to 0.085 a per sq in., at which time the experiment was stopped. A gel-like sludge high in metal ion concentration developed at the gel to metal interface. Gel is in perfect shape. Etched surface is smooth. The addition of dibutyl phthalate had no negative effects on the gel properties.	Dibutyl phthalate is used as a plasticizing agent in cellulose containing lacquers and other composite systems containing cellulose derivatives. The addition of dibutyl phthalate should therefore result in improved gel physical properties.	This gel formulation exhibited the same steady increase in resistance as observed in previous gels containing only hydrochloric acid electrolyte and no nitric acid. The increase in resistance again be attributed to a sludge buildup at the gel to metal interface.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-48	To investigate a cell containing a gel prepared from cellulose acetate and 3 M hydrochloric acid.	L-3052.1 24.0 g cellulose acetate type E-394-30 36.0 cc 20^{o} Be HCl 84.0 cc H_2O	Repeat the same procedure for preparing gel and cell as used for Expt. L-45.	The initial current density was 0.23 a per sq in. with a corresponding potential drop of 2.0 v across the cell. The current steadily decreased until 3 hours later the current density was 0.11 a per sq in. with a corresponding potential drop of 4.2 v. A gel-like sludge developed between the gel and the etch surface of the plate. Removal of the sludge returned the cell to its original, lower resistance with a conductance of 0.23 a per sq in. The gel did not show signs of deterioration during etching. The etched surface is smooth and bright.		The omission of methyl alcohol and dibutyl phthalate from the gel formulation did not eliminate the development of a gel-like sludge high in metal concentration at the gel to metal interface. The resistance of the cell returned to its initial value when the sludge was washed from the gel and plate surface.
L-49	To determine the effect of masking the exposed surface of the gel in a gel cell so that the shrinkage resulting from evaporation will be minimized.	L-3055.1 24.0 g cellulose acetate type E-394-30 24.0 cc 20^{o} Be HCl 9.6 cc 38^{o} Be HNO_3 86.4 cc H_2O	Mix formulation in a Waring Blender. Cast into a 1.5 in. diameter juice glass. Mask the sides of the gel up to 1/8 in. from the gel to plate interface with rubber cement and strip the maskant from the area exposed to the reservoir. Prepare cell and reservoir in same manner as L-34. Add acid solution to petri dish until the exposed gel surface is covered.	The cell stabilized to a current density of 0.16 a per sq in. with a corresponding potential drop of 2.7 to 3.2 v in one-half hour. The cell was disassembled after 13-1/2 hours continuous etching. The gel surface was rough, dry and crusty. The metal ion had diffused completely through the gel. The gel shrank 4.3% in diameter at the interface during etching. The etched surface is rough with approximately 10 mils removed.	The shrinkage of cellulose acetate gels probably results from both evaporation and syneresis. This experiment will mask with rubber cement the surface of the gel exposed to the atmosphere in order to reduce evaporation effects.	Masking the gel surface, which is exposed to evaporation, did not appreciably prevent shrinkage of the gel during the etch action.

Expt No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-50	To investigate the use of drain channels on the gel surface at the gel to plate interface.	L-3058.1 24.0 g cellulose acetate type E-394-30 9.6 cc 38° Be HNO_3 24.0 cc 20° Be HCl 86.4 cc H_2O 20.0 cc CH_3OH 10.0 cc dibutyl phthalate	Mix formulation in a Waring Blender and cast into a 1.5 in. diameter juice glass. Trim the base of the gel until the gel height is 3.5 in. Carve a circular trough around the outside diameter of the gel 3/4 in. below the gel to plate interface. The trough will be parallel to the horizontal plane so that the solution run out from the etch surface will drain down the side of the gel and collect in the trough, rather than stream down the side of the gel into the reservoir and short circuit the gel. Carve a similar trough 1 in. below the first trough. Carve small parallel channels across the gel surface where the gel will etch the anode plate. Run the channels down the side of the gel to the first trough and terminate. Place gel in a pyrex dish and add acid solution 2 M hydrochloric and 1 M nitric acid until solution covers the base of the gel for a height of 3/4 in. Hook a stainless steel cathode into the acid reservoir and place a pickled 321 S.S. anode on the gel surface. Connect cell in series with an ammeter, rheostat and a 6 v direct current power source.	The cell stabilized to 0.18 a per sq in. with a corresponding potential drop of 2.6 v after an initial high current density of short duration. The drain channels eliminated the formation of a meniscus around the periphery of the gel to metal interface. Solution rich in metal ion concentration drained through the channels from the gel to metal interface and collected in the trough. The rheostat resistance was decreased to zero ohms after running the cell for 2 hours with a potential drop of 2.6 v. The potential drop across the cell increased to 5.6 v and the current density increased to 0.69 a per sq in. At this current density and potential drop the plate became warm and the gel started to deteriorate and crack, particularly in the vicinity of the carved channels. The etched surface was uneven because of differential etching in areas adjacent to the channels carved on the gel.	The author has noticed in previous experiments the exudation of solution rich in metal ion concentration from the gel to metal interface. The exudation of solution could result from either capillary rise of solution from the acid reservoir through the gel matrix or result from a squeezing of solution from the gel because of syneresis effects. In this experiment the author proposes augmenting the solution flow by draining the solution as it develops at the interface. In so doing the slow migration of metal ion through the gel matrix could be by-passed, thereby increasing the etch rate	The carving of drain channels on the gel surface where the gel etches the steel plate results in increased flow of metal ions from the gel to metal interface. However the etched surface is uneven and preferentially etched at the plate areas adjacent to the channel furrows on the gel. Drain channels eliminate the meniscus of solution rich in metal ion which collects around the periphery of the gel at the gel to metal interface. High current densities and potential drop across a gel cell results in deterioration and dehydration of the gel electrolyte adjacent to the gel to metal interface.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-51	To prepare a second display sample with a circular etched area 1.5 in. in diameter and approximately 50 mils deep. The initial cut will further investigate deliberate channeling of the gel at the gel to metal interface so as to enhance removal of metal ion products from the gel to plate interface.	L-3064 24.0 g cellulose acetate type E-394-30 9.6 cc 38° Be HNO_3 24.0 cc 20° Be HCl 86.4 cc H_2O 20.0 cc CH_3OH 10.0 cc dibutyl phthalate	Prepare a cell in the same manner as Expt. L-50 except reduce the depth of the channels carved on the gel surface at the gel to metal interface. Disassemble the cell after removing approximately 10 mils from the anode plate and prepare a second cell in the same manner using the same plate but with a fresh gel. Do not carve channels on the second or following gels at the gel to metal interface. Position the consecutive gels on the same surface etched by the first gel. Repeat this procedure with fresh gels until approximately 0.050 in. depth of metal has been removed from the anode plate.	A total of six gels were run in succession to remove an average of 67 mils over a circular area of 1.76 sq in. from a S.S. plate anode. The cut varied from 65 to 70 mils in depth because of the contour in the mold. The etched surface had a few slight mold blemishes but otherwise was smooth and even. The fillet produced by the cut was relatively straight and vertical. The channels carved on the first gel at the gel to metal interface eroded and became larger, resulting in an extremely uneven and rough surface on the etched surface of the anode plate. For this reason, the remaining gels were untouched and left smooth where the gel contacted the anode plate. The second and third gels preferentially etched the high areas on the previously etched surface and removed the roughness. Cells which were assembled with Gels 1, 2 and 3 had a current density varying from 0.11 to 0.18 a per sq in. with a corresponding potential drop of 2.6 to 4.2 v across the cell. The gels were in fair condition after etching, however, the author preferred to use fresh gels for every 10 mils metal removed in order to expedite the making of a sample. Cell force was assembled with a 30 plus 12-ohm resistance in series with the cell and direct current source in order to reduce current density. (Continued on next page).		A total of 0.118 cu in. of metal or 15.82 g of stainless steel were removed from the anode plate. This calculates to 0.628 g equivalents or 60,600 coulombs of theoretical electricity required to oxidize the metal to metal ion. (Assume 73% iron, 18% chromium, and 9% nickle metal composition and that iron is oxidized to ferrous ion, chromium to chromous ion, and nickle to nickleous ion at the anode plate). The addition of ampere-hours actually used to oxidize the metal to metal ion equals 25.5. This is equivalent to 91,800 coulombs of electricity actually used. The ratio of theoretical over actual coulomb usage times 100 for this experiment is equal to 66%, which represents the current efficiency. The total hours of etching equals 120.8 hours which represents an etch rate of 67/121 = 0.56 mils per hour. (Continued on next page).

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
L-51 (con.)				The resulting current density was 0.17 a per sq in. with a corresponding potential drop of 2.0 to 2.4 a. The current remained constant for over 22 hours of continuous etching. *Cells five and six were run with a* 30-ohm resistance in series with the cell and resulted in a steady current of 0.18 to 0.20 a per sq in. The potential drop was 2.1 to 3.4 v across *these cells. Cell five* was etched for 21.5 hours and cell six for 32.5 hours. The gel used in cell number six was soaked in a fresh acid solution of 2 M hydrochloric and 1 M nitric acid for about 8 hours after etching for 22.5 hours. This cell was reassembled with the leached gel and etched for another 10 hours. The metal ion was almost completely leached from the cell after 8 hours of soak. Cell six was the last of the series.		The author believes this experiment is a significant step forward in removing metal from a solid plate with a solid etchant for the following reasons: 1. A steady current and and etch rate was maintained for a continuous 22 hours. 2. The gel has proven itself as a solid electrolyte which can support current over a distance exceeding 3 in. of gel thickness between the anode and cathode plate. 3. A gel electrolyte will preferentially etch micro and macro areas which are the closest to the gel surface, resulting in the ability to remove metal in three dimensions and bring rough surfaces to close tolerances. Future experiments will be designed to improve etch rates and minimize gel shrinkage. The author believes the process and tolerance advantages introduced by gel cells will more than compensate for slow rates of metal removal.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-1	To obtain a preliminary "feel" for electrolytic etching and checkout circuit.	37.5 g CMC 300 cc 6 N HCl 30 cc acetone	CMC and acetone mixed with stirring, then HCl added with continued stirring. Two 2.5 cm square S.S. coupons placed vertically in beaker containing the gel, 1-1/2 inches apart. Voltage applied for 60 minutes without changing external circuit. A 6-volt car battery was used as a power source.	Weight removed = 1.18 g. Thickness removed = 7 mils. Surface of anode smooth and shiny. Gel completely liquefied between electrodes. Time (minutes) / I (amperes) / E (volts): 0 / 2.22 / 2.6 5 / 1.50 / 3.5 10 / 1.15 / 4.0 20 / 1.70 / 3.10 Gel turns to liquid at this point. 30 / 1.70 / 3.10 45 / 1.70 / 3.00 Temperature of gel = 105° F. 60 / 1.80 / 2.90 Strong odor of Cl_2 throughout run.	External resistance satisfactory for preliminary work. Gel system collapses due to heat. Electrolytic etching shows promise. At the end of the run, diffusion products completely filled the space between the electrodes.	No further study planned with this procedure.
M-2	To investigate electrolytic etching of unsupported gels at different applied potentials.	40.0 g CMC 400 cc 3 $\underline{N}$ H^+ and 1 $\underline{N}$ NO_3^- 40 cc acetone	Gelling procedure same as in Expt. M-1. Allowed gel to setup overnight between 1-inch glass plates set in a wooden jig. 4" x 4" 302 sample used as anode, 1" x 1" x 1" gel placed on anode with a honeycomb cathode on top. Voltage applied for 60 minutes. Anode was cleaned for 10 minutes in ultrasonic cleaner. Same circuit as in Expt. M-1.	Run No. 1 Time (minutes) / I (amperes) / E (volts): 0 / 1.6 / 3.0 5 / 1.1 / - 40 / 0.68 / 4.1 50 / 0.60 / 4.2 anodic gassing 50 / 0.49 / 4.0 60 / 0.46 / 4.15 Etch was very irregular, deep mottling made it impossible to measure etch. Diffusion approximately 1/2 inch through gel. Gel oozes liquid at interface with anode.		CMC-gel system holds up satisfactorily with 3 $\underline{N}$ H^+ and 1 $\underline{N}$ NO_3^- over the range of currents employed, that is, up to 1.0 a with a short duration at 1.6 a. If anode is suspended above gel, liquefication is no great problem. Mottled surface results if voltage rises above 2.90

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-2 (con.)			Same as procedure for Run No. 1	Run No. 2 Time minutes / I amperes / E volts 0 / 0.90 / 3.40 15 / 0.90 / 3.40 35 / 0.70 / 3.90 35 / 0.50 / 3.60 40 / 0.50 / 3.85 40 / 0.40 / 3.50 50 / 0.40 / 3.82 53 / 0.39 / 3.90 53 / 0.30 / 3.55 60 / 0.29 / 3.72 Surface same as Run No. 1.	It is felt that the voltage rise across the cell is due entirely to concentration polarization at the anode of the reaction products.	Surface imperfections are caused by imperfect contact between anode and gel. Painting the gel surface with acid before placing the anode is a possibility.
			Same as procedure for Run No. 1.	Run No. 3 Time / I / E 0 / 0.40 / 1.60 10 / 0.40 / 1.70 20 / 0.40 / 1.75 30 / 0.40 / 1.88 40 / 0.28 / 3.00 50 / 0.28 / 3.00 60 increase E to 4.7, I to 0.91 to observe if anodic gassing takes place, none observed. Surface shiny and for most part smooth. Occasional high spots show no etching at all. 3 mils removed.	Since the gel looses spent acid at the anodic interface, this causes discoloration. If anode were above the gel, this would be corrected.	

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-2 (con.)			Anode changed to a 1" x 1" coupon placed on top of gel with honeycomb cathode on bottom.	**Run No. 4** Time (minutes) / I (amperes) / E (volts) 0 / 0.70 / 3.25 10 / 0.72 / 3.22 30 / 0.61 / 3.61 40 / 0.57 / 3.76 50 / 0.50 / 3.98 60 / 0.42 / 4.18 Surface very rough 3 mils removed, crude measurement due to roughness.		
			4" x 4" plate suspended above gel. Used low amperages throughout run. After 30 minutes, reversed positions of anode and cathode with same gel surfaces contacting each electrode.	**Run No. 5** Time / I / E 0 / 0.35 / 2.72 10 / 0.35 / 2.75 20 / 0.34 / 2.82 30 / 0.32 / 2.93 Power off. Slight etch with little mottling. Replaced system with anode now on bottom. Time / I / E 30 / 0.30 / 3.11 40 / 0.29 / 3.11 Liquid diffuses from gel along plate. 50 / 0.29 / 3.11 60 / 0.28 / 3.19 Surface now not so shiny, cannot measure thickness due to positioning in center of plate.	On the second portion of the run, there seems to be little voltage rise compared to previous runs.	

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-2 (con.)			Same gel, same procedure with anode on top except gel is 2 inches thick. After 60 minutes, system was replaced using higher currents.	Run No. 6 Time minutes / I amperes / E volts 0 / 0.37 / 2.32 10 / 0.36 / 2.42 20 / 0.36 / 2.41 40 / 0.35 / 2.60 50 / 0.31 / 2.83 60 / 0.30 / 2.90 Surface texture unchanged except for one unetched spot that corresponds to a low spot on the gel. 1 mil removed. 60 / 1.05 / 4.28 Cl_2 odor noticed immediately, but no anodic bubbling seen. 70 / 1.00 / 4.29 80 / 0.92 / 4.50 90 / 0.74 / 4.90 Gel necks down at anode. Surface mottled as previous. 3 mils removed.	At voltages across the cell lower than 2.90 v, the etching is smooth and slow; above 2.9, faster with severe mottling. Necking down of gel after 60 minutes indicates loss of fluid; most of which probably runs down the sides.	
M-3	To find the optimum voltage across a 1" x 1" x 1" gel.	Same as Expt. M-2.	Gelling same as Expt. M-2. Anode cleaned 10 minutes in ultrasonic cleaner. Gel placed on top of honeycomb cathode. Then anodic surface of gel was painted with acid similar to gel acid. Anode then placed on top. Run No. 1 voltage kept at 2.0–2.5.	Run No. 1 Time / I / E 0 / 0.35 / 2.16 10 / 0.35 / 2.25 25 / 0.33 / 2.50 25 / 0.35 / 2.35 30 / 0.31 / 2.45 37 / 7 / 2.50 37 / 0.27 / 2.50 Second resistor placed in circuit. 45 / / 2.50 45 / 0.21 / 2.22 60 / 0.20 / 2.39 Sample removed, surface same as original, no high spots seen. 1.5 mils removed. Anode replaced after 4 minutes and power reapplied.	High spots on anode are still thought to be due to faulty gel-anode contact.	Satisfactory surfaces are obtained over a 1-hour period if voltage is kept below 2.75 v in the current range from 0.20 a to 0.70 a. Further study will be done to increase current in this voltage range.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-3 (con.)				Time minutes / I amperes / E volts 60 / 0.22 / 2.17 80 / 0.21 / 2.30 90 / 0.20 / 2.41 120 / 0.20 / 2.50 Surface same as end of first portion except for one large high spot and several smaller ones. 2.5 mils removed (total).		
			Hold voltage between 2.50—2.75.	Run No. 2 Time / I / E 0 / 0.70 / 2.50 4 / 0.70 / 2.65 4 / 0.54 / 2.50 8 / 0.51 / 2.65 8 / 0.42 / 2.45 16 / 0.40 / 2.70 16 / 0.30 / 2.40 30 / 0.29 / 2.59 42 / 0.28 / 2.72 60 / 0.20 / 2.69 Surface same as original except for several high unetched spots. 1.5 mils removed.		
M-4	To check out the small battery booster, Allstate Model No. 608.61, as a power source. Also to find how long etching can be maintained before cell resistance builds up to 20 ohms.	Same as Expt. M-2.	Same as Expt. M-3, Run No. 2.	Time / I / E 0 / 0.80 / 2.50 2 / 0.76 / 2.75 2 / 0.62 / 2.50 11 / 0.60 / 2.77 11 / 0.42 / 2.50 35 / 0.40 / 2.82 35 / 0.24 / 2.50 75 / 0.23 / 2.65 Slight necking down at anode; diffusion slow, about 1/16 inch.		Battery booster no better than battery as a power source, amperage too low. Investigate other power sources, such as selinium rectifiers.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-4 (con.)				Time (minutes) / I (amperes) / E (volts): 98 / 0.23 / 2.75 98 / 0.18 / 2.60 130 / 0.18 / 2.65 150 / 0.18 / 2.73 175 / 0.17 / 2.82 Surface very shiny, but slightly mottled. 5.5 mils removed.		
M-5	To check the characteristics of the 12 v — 35 a Selenium P... ifier Fansteel Metallurgical Corp. No. 1211.	Same as Expt. M-2.	Same as Expt. M-3. Voltage range: 2.55—3.25.	Time / I / E: 0 / 1.30 / 3.00 2 / 1.30 / 3.25 2 / 0.89 / 2.85 8 / 0.87 / 2.99 8 / 0.57 / 2.55 34 / 0.56 / 3.00 34 / 0.50 / 2.89 50 / 0.48 / 3.00 Maximum 22 ohms now in circuit. 60 / 0.48 / 3.10 Surface shiny, but slightly mottled. 3 mils removed.	This rectifier puts a higher current through the gel initially, but requires faster cut backs in power due to faster concentration polarization.	It is now obvious that the resistance of the gel is the limiting factor. The largest contributing element to this is reaction product polarization.
M-6	To find the relation between cell resistance and distance between electrodes.	.24 g C.A. 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{N}$ NO_3^- 2.41 g Polyox	The gel was cast as a 1-1/8-inch column. This was placed on a honeycomb cathode, anode plate placed on top. External resistances were set at a certain value and then left constant. Current and voltage was quickly read and power shut off. Anode was removed and cleaned, gel length cut down and and again current and and resistances were read.	For Anodic Plate 6-Inch Gel I = 0.81a, E = 7.30 v R = 9.02 (calculated) 4-Inch Gel I = 0.99 a, E = 6.00 v R = 6.06 ohms For Anodic Honeycomb 4-Inch Gel I = 0.85 a, E = 7.30 v R = 8.59 ohms 3-Inch Gel I = 0.96 a, E = 6.24 v R = 6.50 ohms	After two runs, it was found that the gel was of such nature to preclude a flush fit between gel and anode after the gel was cut. A honeycomb anode was then used to assure a more constant gel to anode contact.	Although a definite trend shows up, the procedure was poor in that the gel was in contact with the cathode at all times and corroded it whenever power was shut off. This caused polarization at the cathode. Furthermore, it is not good practice to let the cell voltage wander through the run.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-6 (con.)				2-Inch Gel I = 1.08 a, E = 5.40 v R = 5.0 ohms 1-Inch Gel I = 1.40 a, E = 2.80 v R = 2.00 ohms 1/2-Inch Gel I = 1.31 a, E = 3.45 v R = 2.63 ohms 1/4-Inch Gel I = 1.56 a, E = 2.60 v R = 1.69 ohms	See Figure 1 for graphical relationship. This particular gel formulation was used simply because it existed in the desired shape. Other gels would have lower electrical resistance and therefore be better suited as an electrolyte, but the resistance to length relationship should be the same for most of these organic semisolids.	Further work
M-7	Repeat Expt. M-6 keeping voltage constant at 5.0 $\pm$ 0.1 volts.	24 g C. A. 120 cc 6 $\underline{N}$ H^+ and 2 $\underline{N}$ NO_3^- 14.3 cc fluorocarbon latex L-242	Same as Expt. M-6 with honeycomb electrodes except the gel will be lifted off the cathode after each determination and both ends will be trimmed for next run. A 64 g weight was placed on top of anodic honeycomb.	5-Inch Gel I = 0.40 a, E = 5.00 v R = 12.5 ohms 4-Inch Gel I = 0.48 a, E = 5.00 v R = 10.4 ohms 3-Inch Gel I = 0.71 a, E = 5.00 v R = 7.05 ohms 2-Inch Gel I = 0.75 a, E = 5.00 v R = 6.66 ohms 1-Inch Gel I = 1.75 a, E = 5.00 v R = 2.86 ohms 1/2-Inch Gel I = 2.05 a, E = 5.00 v R = 2.44 ohms 1/4-Inch Gel I = 3.40 a, E = 5.00 v R = 1.47 ohms	See Figure 2 for graphical relationship.	This shows that not only is contact resistance between electrodes and gel a factor in gel resistance, but the internal resistance of the gel itself is a major factor as well. Approximately 2.34 ohms per inch of electrolyte.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-8	To check the etching characteristics of a stronger acid gel with electrodes closer together.	40 g CMC 400 cc 6 N H^+ and 2 $\overline{N}$ NO_3^- 40 cc acetone	Gelling procedure same as Expt. M-2. Electrolytic cell system the same as M-5 except gel thickness at 1/2 inch.	Time I E 0 1.50 2.50 7 1.38 3.18 Power off as gel begins to liquefy. Gels left in a petri dish for 3 days liquefied by their own accord.		This gel will not hold up under these higher currents.
M-9	Rerun Expt. M-8 with greater distance between electrodes.	Same as Expt. M-8.	Same as Expt. M-8. except gel thickness at 7/8 inch.	Time I E 0 1.20 2.50 1 1.71 2.38 3 Gel accidentally moved, anode fell off. Surface smooth and shiny. 1 mil removed.	The voltage across the gel decreased in the first minute due to gel liquefaction, thereby increasing ion mobility.	
M-10	To rerun Expt. M-9 over a 1-hour period.	Same as Expt. M-8	Same as Expt. M-8.	Time I E 0 1.42 2.50 2 1.50 2.55 Liquid running down sides of gel. 6 1.50 2.56 10 1.49 2.85 10 1.08 2.51 Gel collapsed from anode. This was then lowered to recontact gel. I and E did not change during this maneuver. 15 1.02 2.80 15 0.78 2.51 19 0.69 2.60 Anode had to be lowered again. 30 0.50 2.79 Power off. Total gel shrinkage 3/8 inch on sides with another 1/4-inch depression in the middle. Surface mottled in some places. 2.5 mils removed. This gel when left overnight in cut squares collapsed and ran together.	As the gel collapsed away from the anode, there must have been a liquid layer left because contact did not seem to be broken during the two times the anode had to be lowered.	This gel is not satisfactory at current densities of 1.2 a per square inch.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-11	To check the characteristics of a CMC gel containing only 3 N HCl.	40 g CMC 60 cc methanol 400 cc 3 N HCl	Same as Expt. M-3 using 1/2-inch gel thickness.	Gelling time was not as fast as previous when acetone was used. Slurry was thinner and easier to pour. Very few air bubbles were seen in the mold. After allowing to set overnight, the top of the gel shrunk about 10% from the sides of the mold. Time I E 0 2.70 1.90 Gel begins to liquefy immediately. Voltage across gel is irregular. Tried to keep voltage 3.0 but did not succeed all the time. 7 0.50 3.00 Gel ceases to liquefy. Seems to be dried out more than any previous gel. 10 0.48 3.32 Maximum resistance in circuit; power off. Surface shiny and perfect. 1.5 mils removed.	Too much methanol was used. This resulted in a slight separation of gel and fluid which proved to be mostly methanol (by smell).	The surfaces were the best produced to date. Whether it is due to low concentration, HCl or methanol remains to be investigated. The FeO resulting when the spent gels were immersed in water should also be looked into
M-12	To rerun Expt. M-11 with thicker gel.	Same as Expt. M-11.	Same as Expt. M-3 using 7/8-inch gel thickness.	Time I E 0 2.00 2.30 3 Sharp rise in voltage. 7 Continued voltage fluctuation. Difficult to keep < 3.0 v. Little liquefaction compared to Expt. M-11. 12 0.49 3.07 Maximum resistance now in circuit. 15 0.48 3.21 Power off. Surface shiny and smooth except for several local spots. Dark (black) reaction products at interface of gel and anode, washed easily away. 1.5 mils removed.	For the first 3 minutes, voltage remained constant, then shot up and began to fluctuate. This could be due to accumulation of reaction products at interface that can not diffuse rapidly enough into gel.	Further study should be made to find a gel which can accept reaction products at a faster rate. Production of reaction products at a lower rate may also be tried.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-13	To repeat Expt. M-12 keeping initial current lower to facilitate diffusion of reaction products. When voltage reaches the cut-off level (73.0), shut off power and see if reaction products will diffuse into gel.	Same as Expt. M-11.	Same as Expt. M-11 except that power is shut off intermittently when voltage is 3.0. System is allowed to set, the power reapplied.	Time I E 0 0.92 1.40 10 0.90 1.60 Diffusion 1/16 inch. 11 Rapid voltage rise. Same fluctuations as encountered in 12 0.49 3.10 Maximum resistance now in circuit. Power off for 12 minutes. 12 0.58 1.10 Adjusted to: 12 1.03 1.62 15 Rapid voltage rise. Power off for 21 minutes. 15 0.59 1.10 Adjusted to: 15 1.03 1.68 18 Rapid voltage rise, power off, sample removed. Surface very smooth, but several unetched spots. 1.5 mils removed.		There is insufficient diffusion of reaction products to allow prolonged etching at currents around 1 a/sq in.
M-14	To see how deep an etch can be made by replacing M-11 gel whenever voltages begin to rise sharply.	Same as Expt. M-11.	Mask a square section on a plate with mystik tape Type 7331. When voltage approaches 3.0 v as maximum 22 ohms are in circuit, shut off power, remove gel, wash and measure sample and afix new gel.	Time I E 0 1.80 2.46 Power off, very smooth surface with four small unetched spots. 1.5 mils removed. 2nd Gel 0 1.80 2.20 5 2 mils removed (total). 3rd Gel 0 1.40 2.50 8 3.0 mils removed (total).		In 29 minutes total reaction time, 4.5 mils were removed. Surface remained smooth with very shiny surface. The high spots are of no great problem, for this can be rectified by improved gel surfaces.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-14 (con.)				**4th Gel** After 5 minutes 3.75 mils removed. **5th Gel** After 5 minutes 4.5 mils removed. Reaction stopped. Surface smooth and shiny with several high spots.		If proper indexing can be worked out, there would be no need for masking. Short gel life poses a major problem.
M-15	To reevaluate the etching characteristics of the 3 $\underline{N}$ H^+ - 1 $\underline{N}$ NO_3^- CMC gel with regards to time versus etch relationship. 1/2-inch gel was used.	40 g CMC 40 cc acetone 400 cc 1 $\underline{N}$ NO_3^- and 3 $\underline{N}$ H^+	Same as Expt. M-3, Run No. 2.	**Run No. 1—5 minutes** Time / I / E 0 / 1.52 / 2.60 5 / 1.49 / 2.91 No change in circuit was made. 0.75 mils removed. Surface smooth and dull. **Run No. 2—10 minutes** 0 / 1.59 / 2.50 10 / / 2.89 1.25 mils removed. Surface dull and beginning to mottle. **Run No. 3—20 minutes** 0 / 1.40 / 2.50 20 / 0.48 / 2.80 External circuit had been adjusted to keep voltage within desired limits, 3.0 v. 1.5 mils removed. Surface dull and mottled. **Run No. 4—30 minutes** 0 / 1.70 / 2.50 5 / 1.60 / 2.88 External resistance changed. 10 / 0.88 / 2.58 20 / 0.55 / 2.68 30 / 0.48 / 2.75 1.75 mils removed. Surface dull and very mottled.	Summary of Time Vs Etch T / Mils / Surface 5 / 0.75 / Dull and smooth. 10 / 1.25 / Dull and slightly mottled. 20 / 1.50 / Dull and slightly mottled. 30 / 1.75 / Dull and very mottled.	A gel that contains NO_3^- seems to give a dull finish at best when compared to HCl gel. For the time being, all further work will be conducted with gels containing only HCl.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-16	To investigate the characteristics of a gel containing low H^+ concentration.	40 g CMC 400 cc 0.1 N HCl 40 cc acetone	Standard	Mixture gelled as soon as the acid was poured into the beaker.		At low H^+ concentrations,, the quantity of CMC must be reduced. Further work is planned for low H^+ concentration gels.
M-17	To investigate the characteristics of a gel containing only HNO_3. Refer to results in Expt. M-15.	40 g CMC 400 cc 3 N HNO_3 40 cc acetone	Standard	Maximum resistance almost needed to keep voltage across cell 3.0 v. Time I E 0 0.49 2.65 4 0.44 3.15 Maximum 22 ohms now in circuit. 5 0.44 3.20 Sample removed. No visible etch. Replaced after 1 minute. 5 0.44 3.15 Anodic bubbling noticed. 20 0.46 3.27 Voltage remained steady since reapplication. Anode still has bubbling. Diffusion about 1/8 inch through gel. 30 0.45 3.25 Diffusion about 1/4 inch in some places; not even. 50 0.44 3.30 60 0.43 3.59 Gel much drier than previous ones. Sunk into honeycomb cathode about 1/8 inch. Etch very uneven, not shiny. Not etched in some places. Unreacted gels are more stable than HCl gels. After 4 days, cut gels still retain all their acid.	Initially high cell resistance cannot be explained at this time.	These results tend to prove that HNO_3 will not lend itself to a smooth shiny etch of 302 stainless steel.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-18	To investigate the characteristics of a gel made with cellulose acetate.	24 g C.A. (Eastman Chem.) 120 cc 6 N HC	Dissolved C.A. in required amount of acid in the Waring blender. Heated mixture to 150° F and poured into molds. Electrolytic etching carried out in standard manner.	When gel was poured into molds, there was immediate separation into two opaque layers with a clear liquid layer occurring near the center. The next day, there was only one solid opaque phase. When gel was removed from molds and left in a petri dish for 18 hours, 10 ml of liquid was collected from bottom of dish. Gel breaks apart when cut. Hard and crumbly. Time I E 0 1.80 2.55 1 1.38 5.00 Voltage continually rising. 3 0.46 2.96 Maximum 22 ohms now in circuit. 5 0.43 3.42 10 0.40 4.50 Dark scale of reaction products at anodic interface. Surface smooth and shiny. 1 mil removed.		Gel shows no improvement in etch rate over CMC. Much higher cell resistance. Exploratory work for the immediate future will be confined to CMC gels.
M-19	To investigate a new procedure using gel from Expt. M-11 and allowing voltage to fluctuate without changing external resistance.	Same as Expt. M-11.	Allow voltages to fluctuate without external control.	Time I E 0 2.25 2.50 Gel 6 days old, has a thick liquid layer along bottom of container which oozed from gel. After 45 seconds, sharp voltage rise to 6 v, then dropped back to 5 v and leveled off. 5 1.80 5.00 Voltage and current now oscillating in uniform manner. Volts ± 0.6, amperes ± 0.1. 7 1.75 5.10 Still oscillating. Gel begins to neck down at anode.	Unusually high initial current density. This no doubt caused fast voltage rise as reaction products built up along anodic interface.	

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-19 (con.)				Time I E 10 1.65 5.45 Still oscillating and necking down. 12 1.40 6.15 Anodic bubbling has been noticed. Voltage rising continually. 13 1.23 7.55 Gel has necked down 20%. 2.9 cm @ bottom 2.3 cm @ anode. Surface uneven, shiny in some spots, dull in others. Deepest etch = 4 mils. Thick layer of dark reaction products at anodic interface. These have been washed into a beaker and saved for further study.		
M-20	To rerun Expt. M-19 keeping voltage below 3.0 and shutting off power when it reaches this level instead of changing external resistances.	Same as Expt. M-11.	Maintain constant external resistance and shutoff power at designated point. Allow cell to remain intact.	Time I E 0 4.00 2.50 20 sec. Sharp voltage rise. Power off for 6 minutes. 20 sec 3.30 2.40 35 sec. Sharp voltage rise to 5 v. Power off for 2 minutes. 35 sec 3.30 2.45 50 sec. Sharp voltage rise. Power off for 2 minutes. 50 sec 3.28 2.60 65 sec. Power off for 1 minute. 65 sec 3.28 2.60 80 sec. Power off for 1/2 minute. 80 sec 3.18 2.80 85 sec. Sharp voltage rise. Power off for 1 minute. Gel necking down at anode. 85 sec 3.18 2.80 95 sec. Power off for 1 minute. 95 sec 3.15 3.00	Sharp voltage rise after only 20 seconds is related to fast buildup of reaction products at anodic interface due to high current density.	After the initial voltage rise, the voltage can be made to drop by this procedure. The depth of etch, however, was not materially improved. External resistance would still have to be raised to continue past the present cutoff point.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-20 (con.)				105 sec Power off for 2 minutes. 105 sec 3.13 3.05 115 sec Power off for 3 minutes. 115 sec 3.08 3.15 124 sec Experiment terminated. Surface shiny and smooth. 2 mils removed. Gel is dry and hard at anode compared to before reaction. Thick liquid film on top of this hard gel surface and between this surface and anode.		
M-21	To investigate the previous gel at lower current density.	Same as Expt. M-11.	Standard	Time I E 0 0.30 0.60 15 0.31 0.69 30 0.31 0.78 43 0.179 3.25 Power off. 1.5 mils removed. Surface smooth but not as shiny. The dark layer of reaction products at anodic interface was found to be insoluble in 10 N HCl.	The reaction products found in this experiment are assumed to be the same as all previous products noted before as "dark reaction products at anodic interface".	The fact that some reaction products are insoluble in conc. HCl warrants immediate investigation.
M-22	To conduct an electrolysis with acid but no gel to ascertain the origin of insoluble reaction products found in Expt. M-21.	3 N HCl	Immerse two 1" x 4" S.S. coupon vertically into acid and apply power. Anode and cathode surface area is 1 square inch. Distance between electrodes is 7/8 inch.	Time I E 0 1.00 1.00 Gassing at cathode; none at anode. 10 1.00 1.02 Dark black film detected at anode. Electrolyte dark green. 30 1.01 1.01 Anode completely covered with black film. Power off after 33 minutes. Black film scraped off, collected and dried. 3 mils removed from both sides of anode.		Collected black film from anode will be investigated further.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-23	To conduct a similar experiment as M-22 on a 99% pure Fe sample.	3 N HCl	Same as Expt. M-22 except anode surface area is 3.35 square inches.	Time I E 0 1.01 0.80 No gassing at anode. 10 1.01 0.74 Electrolyte is light greenish yellow. Power off. No film is seen but when cleaned with white towel, a black residue is found. Similar to M-22 but minute in quantity. 2.5 mils removed from both anode surfaces.		None of the film detected on anode could be collected since its quantity was so small.
M-24	To etch the Fe samples with a CMC gel to ascertain whether the minute black film detected in Expt. M-23 will collect at anodic interface.	40 g CMC 40 cc acetone 400 cc 3 N HCl	Standard	Time I E 0 2.30 2.50 Voltage immediately rises. 5 0.51 2.80 8 0.50 3.00 Maximum 22 ohms in circuit. 10 0.43 3.00 Power off. Surface not as smooth as S.S. samples. Deep pitting along perimeter of gel contact. Average 1.25 mils removed. No dark film seen at interface with 10x magnification. Gel seems somewhat drier after reaction than previous gels.	The fast voltage rise cannot be explained at this time.	Acetone as a dispersing agent may be inferior to methanol. This should be checked.
M-25	To check etching characteristic of CMC gel dispersed with acetone (Expt. M-24) with that containing methanol (Expt. M-11).	40 g CMC 40 cc acetone 400 cc 3 N HCl	Standard 1/2-Inch Gel.	Time I E 0 3.60 2.45 1 Fast voltage rise, liquefaction at anode. 3 1.10 2.80 Voltage fluctuating. 9 0.46 3.25 Maximum resistance now in circuit. 10 Power off.	Lower cell resistance than M-11 gels not explained.	M-11 gel shows better surface etching characteristics.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-25 (con.)				Surface shiny but slightly mottled in appearance. High spots of mottling show a copper coloring. After 2 days these gels seem to be more stable than M-11's in 1/4" and 1/2" sheets. The 7/8-inch gel had the top of a petri dish resting on its surface. After 2 days, 10 ml of acid was collected from the bottom of the dish. The thinner gels when cut remained dry after these 2 days.		
M-26	To find a reagent that dissolves the black film collected in Expts. M-20 thru M-22.	Run No. 1 10 N HCl	Add small amount of black precipitate to to reagent at ambient temperature.	Will not dissolve.	Based on solubility and known composition of 302 S.S. Precipitate is believed to be silicon metal.	Further qualitative tests will be made to ascertain black precipitate.
		Run No. 2 4 N H_2SO_4	Same as above.	Will not dissolve.		
		Run No. 3 4 N NaOH	Same as above	Dissolves.		
		Run No. 4	Same as above, NaOH is added to Run No. 1.	Precipitate in Run No. 1 dissolves.		
		Run No. 5 26 Baume NH_4OH	Same as Run No. 1.	Will not dissolve.		
		Run No. 6 48% HF	Same as Run No. 1.			

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-27	To conduct a spot test on collected black film of Expts. M-20 thru M-22 to ascertain if it is Si.	Reference: Spot Test, F. Feigel, Nordeman Publishing Company, 1939, pp. 219 and 258.	(1) Fuse sample with mixture of Na_2CO_3 and Na_2O_2 (1:1) on a Ag foil. (2) Dissolve, melt in HNO_3 in a Pt. crucible. (3) Place one drop of test solution on filter paper with one drop of $(NH_4)_2$ M_oO_4 in an aqueous solution. Warm gently. Add one drop of benzidine, $NH_2C_6H_4C_6H_4NH_2$, in an acetic acid solution. Hold paper over NH_4 fumes. A blue color indicates silicic acid. Run a standard with powdered Si metal as a check.	Both test and standard samples turn blue at conclusion of spot test. Two runs were conducted.	Silicic acid is definitely present. Insolube product is Ti not Si.	Investigation will be conducted as to whether Si can be brought into solution as a positive charged ion or complex. Further tests will be conducted by DAC to ascertain if other metals or compounds are also present in the insolube film. Results from DAC spectroanalysis: Heavy overlay of Ti Fe - Major Cr - Minor Ni - Minor Cu - Trace Mo - Trace Si - Trace Mn - 1 - 2%.
M-28	To find if HF will form insoluble metallic complexes when added to a metallic chloride solution.	Add 24 N HF to 3 N HCl solution containing ions of stainless steel.	See Formulation.	No precipitate can be seen.	The fluorine complexes that result are soluble.	The possibility of using HF in the etchant will be studied.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-29	To ascertain whether a liquid electrolyte containing HF will dissolve Si at the anode.	Run No. 1 3 N HCl 1 N HF	HF comes as 48% solution. Final etchant contains 30 cc 10 N HCl 4 cc 24 N HF 66 cc H_2O Electrolysis conducted same as Expt. M-21, also same electrode dimensions.	Run No. 1 Time I E 0 0.98 2.50 A yellow Fe^{++} stream can be seen coming from bottom of anode. 1 1.05 1.28 Constant observation showed that at 1 minute, green-colored stream replaced yellow one and voltage across cell immediately dropped. 10 1.05 1.28 Black film seen to develop on anode. 30 1.09 1.11 Power off. Surface smooth and coated with black film. 3 mils removed from both anode surfaces.	Run No. 1 In the beginning of the run, perhaps the F^- is complexing with Cr^{++} and Ni^{++} into negative complexes, leaving Fe^{++} to go into solution. After F^- is depleted, the normal S.S. reaction products go into solution.	Further work should be done on HF etchants combined with positive charged complexing agents.
		Run No. 2 3 N HCl 6 N HF	Same as Run No. 1.	0 1.11 1.18 Green-colored stream seen to leave bottom of anode immediately. 10 1.10 1.18 Black film beginning to appear. 22 1.10 1.10 Surface smooth and coated with black film. 3 mils removed.	Run No. 2 Immediate appearance of green reaction products not understood in light of Run No. 1.	
		Run No. 3 3 N HCl 2 N HF	Same as above.	0 1.11 0.92 Immediate green stream from anode. 10 1.11 0.92 Surface covered with black film, cannot tell if amount is less than previous. 1 mil removed.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-30	To find the effect of adding CrO_3 to HCl etchant in regard to Si film.	Run No. 1 3 N HCl 0.5 N CrO_3	Dissolve CrO_3 and carry out electrolysis as in Expt. M-22.	Time I E 0 1.01 1.50 Voltage drops continually. 1 1.08 1.12 Voltage now steadier. 12 1.09 0.99 20 1.09 0.99 Sample removed, cathodic side has no black film, reverse side is lightly covered. 4 mils removed. No gassing seen at anode. 30 1.09 1.08 Cathode side still free of black film, reverse heavily covered. Severe pitting towards bottom of anode. 7 mils removed @ top. 4 mils removed @ bottom.	Although the addition of CrO_3 was not helpful in this etchant, its further use should not be ignored when a suitable etchant has been found.	Run No. 3 showed best surface, yet all had deep pitting. HCl and CrO_3 alone does not bring black film into solution. The addition of HF in Run No. 4 was of no help.
		Run No. 2 3 N HCl 0.1 N CrO_3	Same as Run No. 1.	0 1.11 1.10 Voltage drops to 0.86. 5 1.11 0.86 Sample removed. Light black film seen on both sides. 1 mil removed. 5 1.11 0.86 Cathode bubbling furiously. 10 1.11 0.89 1.5 mils removed. Even etch anode covered on both sides. 10 1.11 0.92 15 1.11 0.98 2 mils @ top. 2.5 mils @ bottom. Heavy black film. 20 1.10 0.96 Continued bubbling at cathode film looks the same. 2.5 mils removed from top. 3.0 mils removed from bottom.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-30 (con.)				Time I E 25 1.10 0.96 Heavy black film on reverse side, also 3.0 mils removed at top. 4.0 mils removed at bottom. 30 1.10 0.95 3.0 mils @ top. 4.25 mils @ bottom. Surface smoother than Run No. 1 but still has numerous deep pits.		
		Run No. 3 3 N HCl 0.4 N CrO_3	Same as above.	0 1.14 0.63 Only a small amount of cathodic gassing. 10 1.14 0.69 No gassing can be seen at cathode, however, solution is very dark. Both sides of anode covered with black film. 2 mils removed top and bottom. 15 No gassing at cathode, I and E constant. 3.5 mils @ top. 3.0 mils @ bottom. 20 4 mils @ top and bottom. 30 5.75 mils @ top and bottom. Voltage and current remained constant. Surface is smooth to the touch but has a multitude of small deep pits.		
	To investigate the addition of HF to the above etchant.	Run No. 4 3 N HCl 0.4 N CrO_3 1 N HF	Same as above.	0 1.04 0.61 Very little cathodic gassing. 11 1.12 0.63 Both anodic surfaces covered with black film. 2 mils removed, top and bottom. 25 1.13 0.65 4.5 mils at top and bottom. 30 1.13 0.66 5.5 mils at top and bottom. Surface		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-31	To investigate the etching characteristics of 5:2 conc. HF and conc. HNO_3.	50 ml HF 48% 24 N 20 ml HNO_3 57.8% 12.4 N	Same as Expt. M-22.	Time I E 0 1.12 0.85 No gassing at cathode. Immediate green color below anode. This diffuses toward cathode much slower than any previous run. 10 1.12 0.87 Green color just reaching cathode. Surface clean. 1 mil removed top and bottom. 20 1.12 0.88 1.5 mils removed. Gassing observed at cathode. 30 1.12 0.82 Surface clean and smooth as original. Not very shiny. 2.75 mils removed. Temperature between electrodes is 135° F.	The HF brings previous black film into solution.	This etchant will be investigated further.
		Run No. 2 5 ml HNO_3 12.4 N 15 ml HF 24.0 N 50 ml H_2O	Same as Run No. 1.	Run No. 2 0 1.01 1.93 Dark brown stream coming from anode. Slight gassing at cathode. 30 1.02 1.89 Surface clean and smooth as original. 2.5 mils removed. Temperature = 105° F 60 1.02 1.98 4.75 mils removed. Surface same as before. 120 1.00 2.22 8.5 mils removed. Temperature = 109° F. 170 0.99 2.50 Etch now uneven. 9.5 mils at top. 10.5 mils at bottom. Surface clean and somewhat rougher than original.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-32.	To investigate the effect of adding HCl to previous etchant M-31, Run No. 2.	5 ml HNO_3 12.4 N 15 ml HF 24.0 N 15 ml HCl 10.0 N 35 ml H_2O	Same as Expt. M-22.	Time I E 0 0.99 2.58 Cathodic gassing. 30 1.00 2.21 3 mils removed. Surface clean and smooth. 30 1.12 0.68 When sample replaced, a dark stream was observed coming from anode. This was not the case in the first 30 minutes. 60 1.12 0.68 Severe anodic gassing. Light black film noticed on anode. Surface smooth and shiny. 12 mils removed at bottom. 10 mils removed at top.	The voltage drop during the second 30 minutes of etch is unexplained.	This etchant warrants further study as a gelled etchant.
M-33	To investigate the addition of CrO_3 to M-32 etchant.	5 ml HNO_3 12.4 N 15 ml HCl 10.0 N 15 ml HF 24.0 N 2.1 g CrO_3 0.4 N (In solution)	Same as Expt. M-22.	Time I E 0 1.02 1.95 Cathodic gassing. 1 Slight gassing at anode. I and E unchanged. 30 1.02 1.95 Surface not shiny; same as original. 3 mils removed. 30 1.13 0.69 No anodic gassing. Same voltage drop as in Expt. M-32. 60 1.13 0.71 Very light black film on anode. Surface not as smooth as M-22. 8 mils removed.	Light black film at anode may indicate that HF is used up at this time. 3 mils removed in first 30 minutes. 5 mils removed in second 30 minutes. This indicates that some polarization has been removed from anode during the cleaning and measuring period between the two segments.	Addition of CrO_3 does not help etchant.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-34	To ascertain at which electrode does polarization occur in the HCl - CMC gel system.	Same as M-11 gel now 13 days old.	Same as Expt. M-3 using 5/8-inch gel. When polarization has set in, use a platinum probe and measure voltage from probe stuck through gel to anode. Repeat measuring voltage from probe to cathode.	After 10 minutes of etching, voltage rose sharply to 4.00 at I = 0.89. Probe in Center E to anode = 1.95. E to cathode = 0.70. Probe 1/4" from Anode E to anode = 1.80. E to cathode = 0.76. Probe 1/4" from Cathode E to anode = 2.00. E to cathode = 0.70. Check on voltmeters: Standard voltmeter across cell reads 1.45 v. Probe voltmeter across cell reads 1.45 v.	It is believed that the voltage from the probe to each electrode does not add up to 4.0 v due to the small contact resistance of the platinum wire probe compared to the larger resistance of each electrode.	Polarization occurs at anode, not cathode.
M-35	To investigate the relationship between probe to electrode voltages and time during etching.	M-11	Same as M-34 except probe is left in center of gel and voltage drop from probe to each electrode is measured at different times.	Time / Cell Voltage / Probe to Anode Voltage / Probe to Cathode Voltage 0 1.40 0.05 1.30 1 1.40 0.05 1.30 3 1.40 0.05 1.30 4 1.75 0.20 1.52 10 3.50 1.65 1.00 12 3.89 1.92 0.75 15 3.89 1.90 0.73 Allowed system to sit for 10 minutes. 15 1.55 0.20 — 16 1.55 0.20 — 17 Rising — 18 4.12 2.12 —	At beginning of etch, polarization is at cathode due to gassing. When anodic polarization begins, cathode polarization drops due to decreased electrolysis.	

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-36	To investigate the gelling and etching characteristics of etchant M-32 in a CMC gel.	5 ml HNO_3 15 ml HCl 15 ml HF 7 g CMC or: 0.89 N HNO_3 2.14 N HCl 5.15 N HF	Standard mixing and electrolysis. Refer to Expt. M-3.	Gel in 1/2-inch mold was firm after 6 hours and removed to a petri dish. After 1-1/2 days, gel leaked acid, about 12-15 ml. Gel in 3/4-inch mold was left there for 1-1/2 days and turned to liquid. 1/2-inch gel was utilized in electrolytic etching. Time I E 0 0.62 2.70 5 0.69 2.59 (Changed ammeters) Reaction products are yellow. 15 0.70 2.28 Voltage irregular, I 0.34 v. Faulty cathodic connection found gel moved accidently. 27 0.63 3.61 Voltage slowly rising. 28 0.59 4.30 Cathode still shows gassing. 30 0.50 5.90 Surface has a layer of light yellowish brown reaction products. These were soluble in ungelled acid. Surface pitted uniformly. 1.5 mils removed. Gel seems drier.	Acid strength too great for CMC. Initial cell resistance higher than HCl — CMC gels.	This system should be investigated further. This is based on the good results obtained in Expt. M-32 as a liquid electrolyte.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-37	To rerun Expt. M-36 at varying current densities.	Same as Expt. M-36.	Same as Expt. M-3, Run No. 1.	Run No. 1 Time I E 0 0.62 0.80 Green-colored reaction products. 8 0.55 2.34 Sharp voltage rise at this point. Voltage now steady. 15 0.54 2.43 30 0.54 2.72 Diffusion one half through gel. 40 0.52 3.05 Surface very rough. Yellowish-brown layer at interface. 1.5 mils removed. Run No. 2 0 0.10 0.40 15 0.11 0.45 30 0.12 0.48 60 0.11 0.55 Diffusion one third through gel. 75 0.10 1.30 Voltage steadily increasing. Power off. Surface has layer of dark. Reaction products insoluble in HCl. Not completely soluble when HF is added. Surface very mottled, can't be measured.	Difference in color of reaction products between M-36 and M-37 unexplained.	Results are poor. Since gel leaked a great deal of acid, it is possible there was preferential HF leaking making results invalid. A lower H^+ conc. gel will be tried.
M-38	To investigate the 3 N HCl–CMC gel of Expt. M-11 on 302 stainless steel.	Same as Expt. M-11.	Standard	Time I E 0 1.10 1.22 5 0.91 3.35 Sharp voltage rise. 8 0.90 3.50 Cut back. 8 0.62 2.89 10 0.50 2.89 15 0.48 3.62 Surface fairly smooth. 1.5 mils removed. Insoluble black film on interface.	Occurrence of black film could be Si. No Ti is present in this steel.	Etch characteristics are the same as 321 steels.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-39	To investigate the HF etchant at a lower H concentration point probe experiment will be run in conjunction with etching investigation.	3 ml HNO_3 0.53 N 15 ml HCl 2.14 N 8 ml HF 2.74 N	Same as Expt. M-35	Gel firm after 3 hours. After 1 day in petri dish, syneresis occurred. However, gel remained firm after 2 days. 3/4-inch gel. Initial color of reaction products is yellow.	Polarization similar to HCl-CMC gels except that it occurs gradually over a longer period of time. This is probably due to the soluble polarization layer compared to the previous insoluble one.	Further work will be done on this system. Results of this run were unsatisfactory. But soluable polarization layers are easier to deal with.

Summary of Results

Current Amp/in^2	Time Min	Cell Voltage	Probe to Anode ,	Probe to Cathode
1.00	0	2.38	0.38	0.80
1.00	2	2.35	0.39	0.80
1.00	4	2.35	0.39	0.80
1.00	7	2.35	0.43	0.81
1.01	13	2.45	0.56	0.81
1.01	14	2.50	0.57	0.85
1.00	16	2.58	0.67	0.85
0.99	19	2.75	0.78	0.93
0.98	22	2.97	1.08	0.94
0.91	27	3.60	1.65	0.98
0.87	34	4.30	2.50	0.95
0.78	40	5.10	3.70	0.90

Etch was mottled and unmeasurable. Reaction products turned green toward end.

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-40	To ascertain the effectiveness of adding Ethylene diamine to previous M-38 etchant with the purpose of complexing metallic ions in a positively charged liquid.	Same as M-39 with 2 ml EDA added.	Standard etching. Gel 3/4-inch thick.	Run No. 2 (see below)	EDA increases the cell resistance.	Etch was not improved. Anodic liquid film difficult to observe. Voltage rise indicates polarization is taking place.

Run No. 2

Time	I	E
0	0.60	2.60
Reaction products are yellow.		
5	0.61	2.72
External circuit changed.		
25	0.48	2.89
30	0.48	2.93

Surface had many small high spots, other than these, surface was smooth.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-40 (con.)	Rerun No. 1 at low current density.	Same as Run No. 1	Same as Run No. 1	Run No. 2 Time I E 0 0.05 0.45 30 0.05 0.48 Reaction products are green. 126 0.055 0.55 Black film at anodic interface, 1 mil removed. 126 0.055 0.47 180 0.050 0.53 Black film at anodic surface. 1.25 mils removed, surface smooth. 180 0.90 1.99 EDA now seen streaming from cathode as a white vapor 195 0.71 4.22 200 0.73 3.69 anode was pressed more firmly to gel 210 heavy dark yellow film similar to M-39 surface severly mottled.		Etch was not improved. Severe mottling occurs if etch is continued after polarization. Same as HCl-CMC gel system.
M-41	Rerun M-40 Run No. 2 at low current density for long time.	Same as M-40 Run No. 1.	Left system over-night at low current density.	Time (hrs) I E 0 0.05 0.50 12 0.055 1.36 Etch very uneven. Maximum etch 6 mils. Diffusion through gel only 3/4-inch gel seems dried out. Surface coated lightly with black film.	Same conclusions as in M-40, Run No. 2. Lower current density does not help etch, merely takes longer to polarize.	Same as M-40, Run No. 2.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-42	To investigate H_2SO_4 as an etchant with regard to black film.	3 M H_2SO_4	Same as M-22	Time I E 0 0.92 2.12 Reaction products are yellow, no anodic gassing. 23 0.93 2.06 Reaction products are now green. No black film, 3 mils removed 60 Solution has a yellow layer below electrodes and green between them. 5 mils removed totally, surface flat but not smooth. Light layer of black film on anode.	As long as reaction products are yellow, the black film, (Ti?) seems to go into solution.	Further work will be done on this etchant due to its power to bring Ti into solution.
M-43	To investigate the effect of EDA in H_2SO_4 etchant.	3 M H_2SO_4 with 2% by vol. EDA	Same as M-22	Time I E 0 0.50 2.41 Heavy anodic gassing reaction products are yellow. 15 0.49 2.41 Continued anodic gassing solution remains yellow. 33 0.49 2.41 Solution was found to be turning green. Light black film found on anode. 1 mil removed.		No further work is planned for EDA-H_2SO_4 etchant.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-44	To investigate the addition of Ethylenediaminetetraacetic acid, Disodium salt in H_2SO_4 etchant.	3 M H_2SO_4 2% by wt. EDTA	Same as M-22	Time I E 0 0.50 1.88 Slight anodic gassing, reaction products are yellow. 15 0.51 1.94 Same observations. 30 0.51 1.94 Very light film, only noticable when sample was wiped with towel. Solution bluish-green. 1 mil removed. Surface smooth, same texture as original.		Not an effective etchant.
M-45	To investigate the characteristics of EDTA added to a $HCl-H_2SO_4$ etchant.	2 M H_2SO_4 2 M HCl 1% wt. EDTA	Same as M-22	Time I E 0 0.99 1.19 green reaction products. 5 1.00 1.26 Black film on anode. 30 1.00 1.26 Severe etching along bottom of anode, light etch elsewhere. Only light black film in evidence.		
M-46 Run No. 1	To investigate DAC etchant No. 3	78.8% 20° Be HCl 21.8% 38° Be HNO_3	Same as M-22	Time I E 0 0.60 0.21 Severe anodic gassing. 27 0.60 0.21 Continued anodic gassing. Heavy black anodic film 6 mils removed.		Of the four Douglas etchants investigated, No. 8 shows the better characteristics.
Run No. 2	To investigate DAC etchant No. 6	18% v 20° Be HCl 18% v 85% H_3PO_4 1% v 38% HNO_3 10% wt. $NaNO_3$ 3% v 38-40° Be $FeCl_3$ 50% v H_2O	Same as M-22	Time I E 0 1.00 1.00 No anodic gassing immediate green color. 30 1.00 0.89 Heavy layer of black film - 5 mils removed.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-46 (con.) Run No. 3	To investigate DAC etchant No. 7	2 liter solution HCl 20° Be 400 ml 2 M HNO_3 38° Be 253 ml 2 M H_3PO_4 85% 144 ml 1 M $FeCl_3 \cdot 6H_2O$ 810.9 g 1.5 M H_2O 324.3 g	Same as Run No. 2	Time I I E 0 1.00 0.89 Slight anodic gassing. 30 0.97 1.72 Thick foam on top of etchant. Heavy black film. Uneven etch. 20 mils removed in some spots. Temperature of electrolyte equals 162° F.		
Run No. 4	To investigate DAC etchant No. 8	2 liter solution HCl 20° Be 400 ml 2 M HNO_3 38° Be 254 ml 2 M H_3PO_4 85% 136 ml 1 M $FeCl_3 \cdot 6H_2O$ 243 g or 131 g $FeCl_3$ 0.4 M H_2O 825 ml	Same as above	Time I E 0 0.19 1.95 No anodic gassing. 30 0.91 1.80 Surface clean and smooth. Reaction products are green.		
M-48 Run No. 1	To investigate the etching characteristics of a H_3PO_4 H_2SO_4 electrolyte obtained from a Russian Journal.	70%vH_3PO_4 15% H_2SO_4 15% H_2O Ref. Zhur. Priklad. Khim. 32:2242 -7 (1959)	Standard liquid electrolysis.	Time I E 0 0.87 2.50 Immediate formation of a yellow film or anode. Slight anodic gassing. 2 0.84 3.02 Voltage reduced. 2 0.51 2.39 Still have anodic gassing. 30 0.49 2.72 Surface very bright 1 mil removed.	The increased etch rate of Run No. 2 probably results from faster diffusion due to decreased viscosity of etchant. The original concentration of acids used in the Russian work is not known.	original etchant results in bright finish but little etching. Run No.2 shows better etching, but still not of sufficient magnitude. Absence of an anodic film is encouraging. Future modification of this etchant are planned.
Run No. 2	Etchant M-48-1 at a lower concentration.	34.5% v H_3PO_4 7.5% H_2SO_4 58.0% H_2O		Time I E 0 0.91 2.20 No anodic gassing. Yellow reaction products. 30 0.88 2.49 Light coating of bubble on bottom-half of sample, bright surface. 3 mils removed.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-48 Run No. 3		14% v H_3PO_4 3% H_2SO_4 83% H_2O		Time I E 0 0.84 2.75 Vigorous anodic gassing. Reaction and products are reddish orange. 30 0.83 2.81 Continued anodic gassing when E reduced to 2.2 v, gassing was stopped. Surface smooth, but not bright 1.25 mils removed.		
M-49 Run No. 1	To investigate characteristics of German etchants similar to M-48 with a cyclic amine added.	55% v H_2SO_4 22% H_3PO_4 21% H_2O 2% Quinoline Ref. Ger. Pat No. 938,402 Jan. 26, 1956	Standard liquid electrolysis.	Time I E 0 0.90 2.14 No anodic gassing. Immediate voltage rise to 2.68 v. This can be decreased by tapping anode. 30 0.85 3.03 Foam covers electrolyte. Surface bright, but covered with a light solubale film. 2 mils removed.		Lower concentration. Seems to improve etch rate, but not materially. Formation of anodic film may rule out this etchant.
Run No. 2		25% v H_2SO_4 10% H_3PO_4 2% Quinoline 63% H_2O		Time I E 0 0.93 1.95 No anodic gassing. Voltage rise slower than Run No. 1. 30 0.91 2.20 Surface smooth but dull. 2.5 mils removed. Foam on top of etchant.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-50 Run No. 1	To investigate modifications of etchant M-48	28% v H_3PO_4 6% H_2SO_4 1% Quinoline 65% H_2O	Standard liquid electrolysis.	Time I E 0 0.93 2.00 No anodic gassing. 30 0.91 2.16 Foam on top of etchant. Light grey film on anode surface smooth and dull. 2 mils removed.	Quinoline seems to be the cause of foam.	No improvement over M-48 Run No. 2
Run No. 2	To investigate the effect of adding HCl	34% v H_3PO_4 8% H_2SO_4 20% HCl 38% H_2O	Standard liquid electrolysis.	Time I E 0 1.05 0.70 Reaction products are green. Black anodic film forms immediately. 15 1.04 0.71 Anode heavily covered with black film. 1 mil removed.	Etchant behaves as a straight HCl electrolyte.	No improvement over M-48 or previous HCl etchants.
M-51 Run No. 1	To investigate a Russian etchant containing chromic acid.	3% $K_2Cr_2O_7$ 20% H_2SO_4 2.5% Na Cl Ref. Vsesoyus Nauch.-Issledovatel Trubuji Inst. 1957 No. 3, III-2	Standard	0 0.97 1.69 No anodic gassing. 30 0.94 1.78 No anodic film surface same texture as original 2 mils removed.		No improvement in etch rate. May have promise in modified form.
M-52 Run No. 1	To investigate an electropolishing electrolyte containing n-Butyl Alcohol.	10-50% v n-Butyl Alcohol (used 25%) 90-50% H_3PO_4 85% (used 75%) Ref. Metal finishing Vol. 59:71 July 1961.	Standard	Time I E 0 0.73 4.32 anodic gassing reaction products are green. 30 0.75 4.12 Continued anodic gassing. Surface clean and bright. 1.5 mils removed.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-52 Run No. 2 (con.)		45% v H_3PO_4 15% n-Butanol 40% H_2O		Time I E 0 0.87 2.77 Slight anodic gassing. 38 0.84 3.01 Surface clean and dull. 2.25 mils removed.		
M-53	To investigate the addition of HCl to etchant M-48 Run No. 2	34% v H_3PO_4 8% H_2SO_4 10% HCl 48% H_2O	Standard	Time I E 0 1.04 0.71 Reaction products are green. Black film forming quickly. 30 0.96 2.48 Heavy black film. Mottled surface. 3.5 mils removed.	Typical HCl reaction products. Ratio of HCl to H_3PO_4 too great.	No improvement
M-54 Run No. 1	To investigate the addition of the 5:2 HF: HNO_3 solution to etchant M-53, in regard to black film.	34% v H_3PO_4 8% H_2SO_4 8% HCl 10% HF 4% HNO_3 36% H_2O	Standard	Time I E 0 0.94 1.97 When external resistor was advanced and then returned to original position: 0 1.02 0.46 Slight layer of dark brown film. Surface shiny but deep gas striations mar surface. 26 mils removed.	Etchant was used right after preparation, the heat of dilution therefore elevated the temperature to approximately 100°F.	Due to accelerated etch rate, this etchant will be studied further. Attempts will be made to stop anodic gassing.
Run No. 2	Reduce H_3PO_4 concentration.	20% H_3PO_4 8% H_2SO_4 8% HCl 10% HF 4% HNO_3 50% H_2O	Standard	Time I E 0 1.02 0.69 Initial voltage drop was much higher, but resistance was advanced and retarded to produce the above voltage drop. Immediate reaction stream after leaving anode is a dark greenish brown. This quickly changes to light green. The dark products adhere to anode. Slight anodic gassing. Still have gassing at E 0.49. 30 1.04 0.61 Surface clean and smooth. 6.25 mils removed.		

APPENDIX D (Continued)

Expt No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-55	To ascertain if etchant M-54 is affected by age.	Same as M-54	Standard	Etchant was made up and stored at room temperature. After 64 hours the following was obtained. Time I E 0 0.92 2.29 No anodic gassing. Resistor run up and down without any results. 30 0.91 2.17 A light layer of reddish reaction products formed only 1.5 mils were removed.	Either the etchant decomposed, or the elevated temperature of M-54 had affected it.	This etchant will be heated and tested.
M-56	To investigate etchant in M-55 at an elevated temperature.	M-55 heated to 140°F	Standard	Time I E 0 1.02 0.91 Voltage dropped to 0.91 from >2 after switch was opened, then closed. 30 1.02 0.89 17 mils removed, deep gas striations.		Results show that temperature has a pronounced affect. Ageing affect not conclusively proved. Further work on this aspect will only be done if etchant proves feasible in a gel.
M-57	To investigate etchant M-56 without HCl.	34% v H_3PO_4 8% H_2SO_4 10% HF 4% HNO_3 44% H_2O or: 5.0 N H_3PO_4 1.5 N H_2SO_4 2.4 N HF 0.5 N HNO_3	Etchant was prepared with external cooling to keep etchant at room temperature. Electrolysis conducted in standard manner.	Time I E 0 0.91 1.99 Voltage did not drop. No anodic gassing. 30 0.96 1.89 No surface film, surface smooth and dull. 2 mils removed.		Etch rate at ambient temperature seems to be same with or without HCl

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-58	To investigate the characteristics of a long etch at a higher current density with etchant M-57.	Same as M-57	Standard	Time I E 0 3.65 2.70 No anodic gassing. 60 3.52 2.70 17 mils removed surface smooth but dull. 90 3.22 3.51 120 3.03 4.11 Anodic gassing, heavy layer of reddish products over entire anode. Surface rough and uneven. Temperature of bath at 170°F. 30 mils removed. There seems to be only a light layer deposited at cathode, this can be easily rubbed off.		Results indicate little plating at cathode. Electrolyte then becomes loaded with products and etch rate is reduced and non-uniform. This is not encouraging for a gelled electrolyte.
M-59	To ascertain if etchant M-57 can be gelled in CMC.	100 ml etchant 12 ml CH_3OH 12 g CMC	Electrolysis carried out similar to M-3. Gel 1/2-inch thick.	Time I E 0 0.50 2.25 12 0.28 7.90 15 0.25 8.25 Anode was covered with a heavy reddish brown layer of products. These were soluble in etchant 0.25 mils removed.	Since the interfacial build-up proved to be soluble, the problem is diffusion. Are the products undiffusable, or are they negatively charged?	System proved unsatisfactory. No diffusion.
M-60 Run No. 1	To find a lower CMC: Acid ratio for the previous gel in order to improve the diffusion properties. This will be checked by a long etch at low current density.	100 ml M-57 9 g CMC 11 ml Acetone		Gel sets up rapidly stable after 48 hours.		Run No. 1 produces a good gel. Its etching characteristics are, however, unsatisfactory. No further work is planned on this acid-gel system.
Run No. 2		100 ml: 8 g CMC 10 ml Acetone		Gel sets up rapidly. Remains firm when cut but beings to liquify after 48 hours		
Run No. 3		100 ml: 7 g CMC 9 ml Acetone		Gels enough to remove from mold, but slowly loses its shape		

APPENDIX D (Continued)

Expt No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-60 (con.) Run No. 4		100 ml: 6 g CMC 8 ml: Acetone		Did not gel. Gel from Run No. 2 was used in following test. Time I E 0 0.10 0.38 10 hrs. 0.05 8.00 A thick dark reaction layer accumulated at anodic inter-face. This was soluble in etchant No. M-54, was not check for in M-57. Etch was insignificant, only produced a mottled texture. Only a very light green color diffused into the gel.		
M-61 Run No. 1	To gel acid M-54 to ascertain if the HCl improves the diffusion of reac-tion products.	100 ml acid 54 to 10 g CMC with 12 ml methanol	Standard	Gelled too quickly to be proved.		There seems to be no difference between acetone and methanol as a dispersing medium for CMC. Acetone will hence-forth be used. No improvement of M-60. Reaction products will not diffuse. Etchant not satisfactory.
Run No. 2		100 ml: 9 g CMC with 11 ml acetone		Pourable, gels within 1/2 hrs. Stable after 36 hours.		
Run No. 3		100 ml: 8 g CMC with 10 ml methanol		Pourable, gels within 11/2 hrs. Stable after 24 hours, begins to liquify after 36 hrs. The following test used gel from Run No. 3, 2 hrs. after gelling. Time I E 0 1.00 1.50 1-1/2 0.87 3.11 Voltage rises slowly. 4 0.61 6.20 15 0.29 10.50 Anode was hot to the touch, gel was beginning to collapse. Heavy greenish brown layer adhered to plate when this was removed from gel. This was soluble in etchant. 0.75 mils removed. Mottled surface texture.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-62	To investigate the etching characteristics of DAC etchant No. 8 in a CMC gel (Refer to M-46)	100 ml DAC No. 8 8 g CMC 10 ml acetone	Standard	Gelled in 1 hour. Time I E 0 0.95 2.21 4 0.92 2.41 7 0.91 2.70 White fumes coming from cathode. 16 0.89 2.79 30 0.88 3.01 2 mils removed, surface mottled with some high spots. No insoluble layer.		Further work will be done on this system.
M-63	To investigate the system in M-62 at low current density over longer periods of time.	Same as M-62	Standard	Time I E 0 0.10 0.44 6 hrs. 0.09 1.57 Black, insoluble layer at anodic interface. Etch very irregular. 4 mils at deepest point. Gel seemed to have collapsed in center.		The appearance of insoluble products preclude any continuous etching with this system as it now stands. Further work on adjustments will be done.
M-64	To investigate the characteristics of a straight NaCl electrolyte.	1.5 N NaCl	Standard liquid electrolysis.	No current or voltage readings were recorded. After 15 min. Anode had severe pitting, but no surface etch. $Fe(OH)_2$ and $Cr(OH)_3$ formed as precipitate.	The hydroxyl precipitate formed as H^+ was depleted.	Since metal removal has taken place, further work will be done on this system.
M-65 Run No. 1	To investigate the NaCl electrolyte with CH_3COOH added.	1.5 N NaCl 1.0 N CH_3COOH	Standard	No current or voltage readings where recorded. Voltage ~ 3.0. Current ~ 1.0. After 45 minutes, severe pitting resulted.		This system is not promising.

APPENDIX D (Continued)

Expt No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-65 (con.) Run No. 2		1.5 N NaCl 5.0 N CH_3COOH		After 10 min. pitting was observed and run terminated.		
Run No. 3		0.75 N NaCl 15.6 N CH_3COOH or 50% by vol CH_3COOH	Standard	After 20 min., severe striations on lower half of anode. No metal removed from top. Light pitting throughout.		
M-66	To investigate if polarization can be stopped or retarded by placing the anode in a horizontal position above a liquid electrolyte.	60 ml HCl 100 ml HF 40 ml HNO_3 300 ml H_2O	A two compartmented cell was made from Neoprene. One compartment for anode the other for cathode. A liquid head will be maintained in cathode side.	Time I E 0 1.03 1.50 15 1.03 1.47 30 1.03 1.49 Gas bubbles observed under anode. Power off light black film on surface, etch uniform and smooth. 2 mils removed.	When electrolyte becomes loaded with salts, dissolved gas will precipitate from the liquid.	Further work will be done to determine the feasibility of this cell as a research tool.
M-67	Repeat M-66 with etchant M-54 in diluted form. Cell will be provided with vent for gas release.	50% v H_2O 6% H_2SO_4 27% H_3PO_4 6% HCl 3% HNO_3 8% HF	Same as M-66 with vent hole provided and entire cell tipped at 20° angle toward vent.	Time I E 0 2.50 3.42 30 2.62 3.31 Steady stream of gas leaving vent. 45 2.57 3.44 50 2.56 3.46 12-13 mils removed. Surface as severe gas striations. Surface smooth other than this. Surface clean, no reaction products adhere.	The original M-54 etchant had severe anodic gassing. This seems to be the case for this more dilute form also.	These tests show that reaction products will diffuse by convection currents there by leaving anode unpolarized.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-68 Run No. 1	To ascertain if CMC resin acts as an inhibitor to the anodic reaction.	60 ml M-67	M-67 etchant will be used as bases for test. Electrolysis is carried out in standard manner of a liquid electrolyte.	Time I E 0 0.99 2.20 Power shut off, then on instantly. 0 1.07 0.91 2 0.99 2.20 Power off, then on. 2 1.07 0.91 Light black film after 1 min., no film after 2 min.	The voltage drop phenomenon is not usual for this etchant.	A further test willl be conducted on the more standard 4 N HCl - 2 N HNO_3. Based on the complicated results of this test, the CMC does not inhibit the anodic reaction.
Run No. 2		60 ml etchant 0.5 g CMC 1.0 ml acetone		Time I E 0 1.00 2.10 Power off then on. 0 1.02 1.04 Light film after 1 min. 2 1.00 2.10		
Run No. 3		60 ml etchant 1.0 g CMC 2.0 ml acetone		Time I E 0 0.97 2.44 Power off, then on. 0 1.05 0.95 2 0.95 2.25 Power off, then on. 2 1.06 1.00 4 0.95 2.30 No black film.		
Run No. 4		60 ml etchant 3.0 g CMC 4.0 g acetone		Time I E 0 0.97 2.32 Power off, then on. 0 1.06 1.09 20 sec. 0.95 2.38 Power off, then on. 20 sec. 1.04 1.13 25 sec. 0.95 2.39 No black film.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretations of Results	Conclusions and Recommendations
M-68 (con.) Run No. 5		60 ml etchant 5.0 g CMC 7.0 ml acetone		Time I E 0 0.97 2.22 Power off, then on. 0 1.03 1.05 10 sec 0.97 2.30 Power on, then off. 10 sec 1.03 1.06 12 sec 0.93 2.31		
M-69 Run No. 1	To rerun the previous test on a more simple etchant.	6 $\underline{N}$ H 2 $\underline{N}$ NO_3^- 60 ml 6-2 acid	Same as M-68 except each run will last 10 min. The same electrode surface will be used as in M-68.	Time I E 0 1.10 0.61 10 1.10 0.58 3.25 mils removed.		No change in runs 1 and 2. Therefore CMC does not inhibit the reaction as more CMC is added, the diffusion is slowed and therefore reaction is slowed. No chemical inhibitation is evidenced.
Run No. 2		60 ml etchant 0.5 g CMC 1.0 ml acetone		Time I E 0 1.09 0.61 2 1.08 0.66 12 1.10 0.51 3.25 mils removed		
Run No. 3		60 ml etchant 1.0 g CMC 2.0 ml acetone		Time I E 0 1.10 0.62 10 1.11 0.60 2.75 mils removed. Surface now very rough.		
Run No. 4		60 ml etchant 3.0 g CMC 4.0 ml acetone		Solution gelled in 3-4 min. A new anode is etched. Time I E 0 1.10 0.70 5 1.10 0.79 Very little diffusion is taking place. 10 1.09 0.81 No diffusion beyond 1/8-inch from anode 1.25 mils removed.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-70 Run No. 1	To investigate a variation of a salt etchant for stainless steel found in the Italian Journal Metital 48, 324-326 (1956)	0.5 N $(NH_4)_2 S_2O_8$ (Ammonium persulfate) 0.5 N $NaBrO_3$ (Sodium Bromate) Aqueous solution	Standard liquid electrolysis.	Time I E 0 0.88 2.72 Anodic gassing, no cathodic gassing. Above 3.5 volts, cathodic gassing commences 30 0.89 2.45 Cathodic gassing has just started. Dark reddish brown products are being producted by electrolyte itself. As temperature is elevated by electrolysis, the electrolyte decomposes or reactes with itself. Anode clean and smooth. 1.75 mils removed. Deep pitting or edges, none on surface. Nitrous oxide seems to evolve from electrolyte.	The violent reactions of Run No. 1 were mostlikely set off by the heat generated by Run No. 1's higher current density.	No further work is planned with this salt system.
Run No. 2		0.1 N $NaBrO_3$ 1.0 N $(NH_4)_2 S_2O_8$		Time I E 0 0.89 2.41 Gassing at both electrodes. 0 0.61 2.23 No cathodic gassing. Solution turns reddish brown. 30 0.61 2.31 Continued anodic gassing, no violent reaction similar to Run No. 1. Solution is a clean reddish orange. 1.5 mils removed. Surface clean and smooth, no pitting on sides.		
Run No. 3		1.0 N $(NH_4)_2 S_2O_8$ 0.1 N $NaBrO_3$		Time I E 0 0.59 3.00 Equal electrode gassing. 30 0.61 3.18 Zero mils removed. Hardly any change in surface texture.		

APPENDIX D (Continued)

Expt No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-71 Run No. 1	To rerun M-69 with cellulose acetate	60 ml 6-2 acid 0 g CA	Same as M-69	Time / I / E 0 / 1.03 / 0.55 10 / 1.03 / 0.55 1.75 mils removed.		The addition of CA to etchant has no effect untill CA slurry begins to gel This aspect may be investigated further when more time is available.
Run No. 2		60 ml acid 0.5 g CA		Time / I / E 0 / 1.05 / 0.59 10 / 1.06 / 0.56 1.75 mils removed. Anodic gassing observed.	Anodic gassing was observed throughout remainder of Runs.	
Run No. 3		60 ml acid 1.0 g CA		Time / I / E 0 / 1.06 / 0.60 10 / 1.06 / 0.52 2.00 mils removed.		
Run No. 4		60 ml acid 2.0 g CA		Time / I / E 0 / 1.03 / 0.60 10 / 1.02 / 0.59 1.75 mils removed. Slurry separates into two layers.	Separation into two layers observed in Remained of run. Electrolysis is conducted through this central liquid layer.	
Run No. 5		60 ml acid 4.0 g CA		Time / I / E 0 / 1.05 / 0.61 10 / 1.07 / 0.58 1.75 mils removed.		
Run No. 6		60 ml acid 6.0 g CA		Time / I / E 0 / 1.05 / 0.63 10 / 1.06 / 0.59 1.75 mils removed.		
Run No. 7		60 ml acid 8.0 g CA		Time / I / E 0 / 1.04 / 0.65 10 / 1.05 / 0.62 1.75 mils removed.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-72	To investigate the effect of reversing polarity on HCl-CMC system.	3 N HCl 12:100 CMC:Acid	M-3, Run No. 2. Standard procedure with reversal of current at 1-minute and 0.5-minute intervals.	Time / I / E 0 / 1.00 / 1.24 1 / 0.95 / 1.55 1.5 / 1.00 / 1.35 2.5 / 0.95 / 1.5 + At this point voltage across anodic plate begins to rise rapidly. Reversing procedure is accelerated. When plate is now made cathodic, the voltage continues its rise for a second, then as H_2 is liberated and bursts against the plate; the voltage takes a sharp drop, this is accompanied by a cracking noise. After 40 minutes a heavy, black, insoluble film collects at plate interface. Surface severely mottled. 1.75 mils removed at deepest etch.		This procedure has no effect on anodic solution. Insoluble film is perhaps affected, but polarization continues.
M-73 Run No.1	To ascertain the effect of superimposing AC on regular DC to produce an electronic reversal of polarity.	Same as above.	DC circuit same as previous. AC circuit consists of a power-stat transformer (230 v 60cps, 9A) connected to 110 v source. Two capacitors, 10μF and and 4μF are set in parallel to block the DC from flowing through power stat. An oscilloscope is connected across electrolytic cell to observe the wave form.	DC Only Time / I / E 0 / 0.99 / 0.82 5 / 0.98 / 0.94 8 / 0.98 / 1.02 10 / 0.81 / 2.5 + Voltage rising rapidly, power off. Black film, surface smooth, 1 mil removed.		At these voltages and frequency, no improvement is noticed.
Run No.2				AC – DC Time / DC I / DC E / AC E 0 / 0.99 / 0.78 / 50 3 / 0.99 / 0.82 / 50 9 / 0.98 / 1.00 / 50 11 / 0.95 / 1.21 / 50 12 / 0.91 / 2.50 / 50 Voltage rising rapidly. Surface smooth, covered with black film. 1.25 mils removed.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-73 Run No. 2 (con.)				Wave Form:		
Run No. 3	To ascertain the effect of a higher AC voltage across cell with respect to DC voltage.	Same as previous.	Increase AC and decrease DC.	DC Only Time / I / E 0 / 0.57 / 0.65 11 / 0.58 / 0.71 17 / 0.58 / 0.80 19 / 0.57 / 0.83 25 / 0.55 / 1.06 26 Rapid voltage rise. Black film, surface has multitude of high spots. 1.5 mils removed.		
Run No.4				AC–DC Time / I (DC) / E (DC) / AC/E 0 / 0.57 / 0.58 / 80 15 / 0.57 / 0.75 / 80 23 / 0.57 / +3.5 / 80 Surface same as Run No. 3, 1.25 mils removed.		
M-74 Run No. 1	To ascertain the effect of superimposing AC over DC on a HF-CMC system.	65 ml H_2O 25 ml HF 10 ml HNO_3 12 g CMC	Same as M-73.	DC Only Time / I / E 0 / 0.88 / 2.29 3 / 0.86 / 2.41 5 / 0.83 / 2.72 7 / 0.78 / Rising No insoluble film, brown viscous solution in interface. Surface mottled. 0.50 - 1.0 mils removed.		Superposition of AC has no effect.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-74 (con.) Run No.2				AC–DC Time / DC I / DC E / AC E 0 / 0.89 / 2.03 / 50 4 / 0.89 / 2.21 / 50 6 / 0.81 / >3.0 / 50 Surface mottled. 0.50 - 1.00 mils removed.		
M-75 Run No.1	To ascertain the properties of a Ni electroplating electrolyte as a regenerative system for Rene 41.	100 ml H_2O 12.0 g $NiSO_4 \cdot 6\ H_2O$ 4.5 g $NiCl_2 \cdot 6\ H_2O$ 3.0 g H_3BO_3 Ref: Practical Nickel Plating, The Int'l. Nickel Co., p. 13.	Standard liquid electrolysis.	pH of electrolyte 2 DC Only Time / I / E 0 / 0.45 / 2.87 21 ohms in circuit, no electrode gassing. 5 / 0.45 / 3.08 Slight cathodic gassing. 20 / 0.45 / 3.08 30 / 0.45 / 3.10 Slight anodic gassing. A brown, insoluble layer covered anode. 0.75 mils removed, 0.19 g removed.		Superimposing AC has no effect on this system. Electrolyte is non-regenerative.
Run No.2				AC–DC AC was superimposed at 100 v; no change in observations other than a small reduction in voltage drop across cell. Brown film not soluble in HCl, soluble in HF.		
M-76	To investigate the characteristics of another nickel electroplating bath on Rene 41.	100 ml H_2O 12.0 g $NiSO_4 \cdot 6\ H_2O$ 1.5 g NH_4Cl 1.5 g H_3BO_3	Standard liquid electrolysis.	Voltage will be maintained below 2.5 v. Time / I / E 0 / 0.20 / 2.50 Gas forms on cathode, but does not evolve. 30 / 0.19 / 2.49 Cathodic gassing, slight anodic gassing. 0.10 g removed.		Electrolyte inferior to M-75. No further work will be done on this electrolyte.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-77 Run No. 1	To ascertain the behavior of Electrolyte M-75 in a CMC gel on Rene 41.	100 ml M-75 11 g CMC 13 ml acetone	Stainless steel plate was used for a cathode upon which gel was placed. Rene 41 1 x 4" strip on top of gel was anode.	Gel became firm after 5 minutes; remained thus after 4 days. Gel retains consistency, but is completely in-elastic. Time I E 0 0.19 4.15 Gassing at cathode. 8 0.15 4.21 12 Inadvertantly squashed gel.		System unsatisfactory, non-regenerative and not enough electrical conductivity.
Run No. 2				Run No. 2 0 0.05 2.60 1 0.04 2.49 Cathodic gassing. 20 0.04 2.55 40 0.04 2.55 Gel begins to collapse and flow from anode. Surface of anode unchanged. 0.05 g removed.		
Run No. 3			Run No. 3 Low current density for long duration. Resistance in circuit changed to a potentiometric one.	Run No. 3 0 0.01 2.30 14-1/2hrs 0.00 2.33 Gel shrank from anode so that only a small section in center remained in contact. 1.25 mils removed with 4.25 mils in center. No plating on cathode.		
M-78	To investigate a Nickel Electro-refining electrolyte on Rene 41.	100 ml H_2O 11 g $NiCl_2 \cdot 6H_2O$ = 6 g $NiCl_2$ 2 g H_3BO_3 3.5 g Na_2SO_4 3.5 g NaCl	Standard liquid electrolysis with stainless steel cathode.	Time I E 0 0.36 2.45 No electrode gassing. 2 0.35 2.46 Stagnant gas on cathode. 18 0.35 2.46 Cathodic gassing.		System not satisfactory due to precipitation.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-78 (con.)				Time I E 24 0.32 2.52 35 0.30 2.54 70 0.28 2.59 Anode covered with heavy brown film. White precipitate floating in electrolyte. 1 mil removed. Surface smooth.		
M-79	To investigate Electrolyte M-75 on Inconel X.	Same as M-75	Standard liquid electrolyte with stainless steel cathode. Inconel X anode.	Time I E 0 0.18 2.50 No electrode gassing. 9 0.19 2.45 Stagnant gas on cathode. 30 0.20 2.43 No surface film, no surface etch; merely close. uniform pitting. 0.20 g removed.		Electrolyte is better suited to Inconel than to Rene. Not worth gelling at this time.
M-80	To investigate Electrolyte M-78 on Inconel X.	Same as M-78	Standard liquid electrolysis.	Time I E 0 0.68 2.40 Violent cathodic gassing. 2 0.70 2.31 15 0.71 2.31 30 0.72 2.30 No surface film, but white precipitate, 0 mils removed, uniformed pitting 0.29 g removed. Ppt. dissolves in HF.	As electrolysis proceeds, conductivity increases.	Further work will be done to stop precipitation and cathodic gassing. Due to weight of metal removed, electrolyte may have possibilities.
M-81	To ascertain if HF added to M-80 will dissolve ppt.	90 ml H_2O 10 ml HF 11 g $NiCl_2 \cdot 6\,H_2O$ 2 g H_3BO_3 3.5 g Na_2SO_4 3.5 g NaCl	Standard liquid electrolysis stainless steel and Inconel X.	Time I E 0 0.97 2.50 Vigorous cathodic gassing 5 0.99 2.40 21 1.10 2.06 30 1.13 2.00 No ppt. formed, surface clean and smooth except for pitting near edges. 1.5 mils removed.		Results encouraging. Further work will be done to improve etch, reduce gassing and increase conductivity.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-82	To ascertain if an increase in Ni content will decrease anodic pitting.	85 ml H_2O 15 ml HF 24.4 g $NiCl_2 \cdot 6H_2O$ = 6 g Ni 2 g H_3BO_3 3.5 g Na_2SO_4 3.5 g NaCl	Standard liquid electrolysis, stainless steel and Inconel X.	Time I E 0 0.97 2.50 Vigorous cathodic gassing. 2 min 1.21 1.91 3 min 1.22 1.73 7 min 1.22 1.72 30 min 1.22 1.72 Surface uniform, clean and crystalline in texture. 2.25 mils removed. 0.59 g removed. 74.4% current eff.		Increasing Ni content increases etch rate, increases conductivity, and produces a uniform but crystalline etch.
M-83 Run No.1	To ascertain the effect of removing NaCl from M-82.	85 ml H_2O 15 ml HF 24.4 g $NiCl_2 \cdot 6H_2O$ 2 g H_2BO_2 3.5 g Na_2SO_4 0 g NaCl	Standard liquid electrolysis.	Time I E 0 1.82 2.50 Vigorous cathodic gassing commences at 0.04 volts. 15 1.85 2.43 30 1.85 2.40 Surface clean, uniform and crystalline. 4 mils removed. 0.93 g removed. 0.41 g plated.		Removing NaCl increases etch rate.
Run No.2	To ascertain the effect of removing H_3BO_3 from Run No. 1.	85 ml H_2O 15 ml HF 24 g $NiCl_2 \cdot 6H_2O$ 3.5 g Na_2SO_4		0 0.80 2.25 Vigorous cathodic gassing. 5 0.88 2.08 7 1.08 2.55 9 1.11 1.51 20 1.10 1.51 30 1.10 1.51 Good plate on cathode. 0.43 g removed. 0.20 g plated. 2.0 mils removed. Surface clean, crystalline.		Removal of H_3BO_3 produces a more pronounced conductivity rise, but does not show a commensurate rise in etch rate.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-84	To ascertain if substitution of NH_4F for HF will stop cathodic gassing in above electrolytes.	100 ml H_2O 10 g NH_4F 24.4 g $NiCl_2 \cdot 6H_2O$ 2.0 g H_3BO_3 3.5 g Na_2SO_4	Standard	Time I E 0 0.71 2.52 No electrode gassing. 1 0.74 2.43 3 0.86 2.14 White ppt. forming. 7 0.91 2.05 30 0.95 1.96 Anode covered with white ppt. Very uneven etch. 0.37 g removed. 0.73 g plated on cathode.	Uneven etch, no doubt caused by adhering ppt. cathode wt. gain due to deposition of electrolyte.	The substitution stopped gassing but brought back ppt., reduced etch rate and conductivity.
M-85	To ascertain if ppt. is due to Na_2SO_4.	100 ml H_2O 24.4 g $NaCl_2 \cdot 6H_2O$ 2.0 g H_3BO_3 3.5 g NaCl	Standard	Time I E 0 0.79 2.45 Slight cathodic gassing. 1 0.87 2.19 3 0.89 2.11 11 0.96 1.94 30 1.00 1.85 Still have slight cathodic gassing. White ppt. adhering to anode, very rough, uneven etch. 0.3 g removed.		Precipitate not due to Na_2SO_4; its removal lowers etch rate and conductivity. Removal of NH_4F not evaluated.
M-86	To ascertain the results of removing H_3BO_3.	100 ml H_2O 10 g NH_4F 25 g $NiCl_2 \cdot 6H_2O$ 3.5 g Na_2SO_4 3.5 g NaCl	Standard	Time I E 0 0.90 2.05 Very slight cathodic gassing. 20 1.02 1.78 30 1.05 1.71 Still have ppt. but not as much. Surface same as previous. 0.5 mils removed.		Removal of H_3BO_3 increased etch rate and conductivity over M-84, but allowed some cathodic gassing. Decrease in ppt. is encouraging.
M-87	To ascertain the results of removing NH_4F from M-86.	100 ml H_2O 25 g $NiCl_2 \cdot 6H_2O$ 3.5 g Na_2SO_4 3.5 g NaCl	Standard	Time I E 0 0.80 2.32 Vigorous cathodic gassing. 30 0.85 2.23 No surface etch, merely uniform pitting. Precipitate collects on bottom, does not adhere. 0.39 g removed.		Removal of NH_4F not advantageous.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-88	To ascertain the effect of adding Ni as a sulfate in place of chloride.	100 ml H_2O 10 g NH_4F 25.3 g $NiSO_4 \cdot 6 H_2O$ = 6 g Ni 3.5 g Na_2SO_4 3.5 g NaCl 0 g H_3BO_3	Standard	The addition of NH_4F to $NiSO_4 \cdot 6 H_2O$ in aqueous solution, results in a precipitate.		Not satisfactory.
M-89 Run No.1	To ascertain if an increase in HF concentrate will increase etch rate over M-83, Run No. 2.	70 ml H_2O 30 ml HF 25 g $NiCl_2 \cdot 6 H_2O$ 3.5 g Na_2SO_4	Standard	Time I E 0 1.01 1.65 Vigorous cathodic gassing. 30 1.08 1.53 0.49 g removed. 3.5 mils removed.	Note: External circuit setting constant throughout nickel electrolyte runs.	Electrolyte gases at cathodic but has best etch rate in Inconel series.
Run No.2			Reverse side of anode taped with Mystic tape.	0 1.12 2.50 80 1.19 2.32 Etch smooth in center, pitted near edge with very deep cut along liquid-air interface. 5.5 mils removed. 1.46 g removed.		
M-90	To ascertain the etching characteristics of the previous electrolyte in a CMC gel.	70 ml H_2O 30 ml HF 25 g $NiCl_2 \cdot 6 H_2O$ 3.5 g Na_2SO_4 11 g CMC 13 ml acetone	1/2-inch gel 3 x 3/4" laid on S.S. honeycomb. Inconel X anode on top.	Solution gels slowly but remains firm and dry after 7 days. Gels overnight. Time I E 0 1.30 2.00 5 1.29 2.01 8 1.09 2.50 10 1.01 2.79 11 0.98 2.91 12 0.94 3.01 13 0.91 3.09 15 0.87 3.23 20 0.70 3.71 30 0.52 4.25 1.75 mils removed 0.41 g removed. Surface clean, smooth except for several high spots. Gel dries out.	Polarization due to conc., not to surface effects as previously encountered.	Gel cuts at a fast rate initially. Then 1.75 mils in first 30 minutes at 0.58 asi. Than 1.25 mils per hour for 3 hours at 0.89 asi. This slows to an even lower rate if left for 17 hours. However, gel remains intact and etching continues. High current density of Run No.3 seems to be too high. On the other hand, Runs No. 2 and No.4 seem to be too low.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-90 (con.) Run No.2			Lower current density for longer time.	Time I E 0 0.40 1.69 Power off, then on. 0 0.65 1.22 30 sec 0.40 0.98 4 0.40 0.98 15 0.36 1.01 27 0.32 1.08 52 0.28 1.11 Clamp on anode realigned. 52 0.32 1.08 87 0.24 1.18 120 0.18 1.22 155 0.16 1.28 180 0.15 1.28 Gel remains firm and dry. Surface uniform but rough texture. 2.5 mils removed. 0.72 g removed.		
Run No.3			Higher current density for 3 hours.	Time I E 0 2.00 2.37 12 0.64 6.20 27 0.38 7.00 42 0.28 7.22 61 0.20 7.44 80 0.17 7.59 90 0.16 7.62 110 0.14 7.70 121 0.13 7.75 140 0.12 7.70 180 0.15 7.75 Surface smooth except for several small, high spots at one end. 3.75 mils removed. 0.84 g removed.		
Run No.4			Low current density for 17-1/2 hours.	Time I E 0 0.40 0.86 Surface uniform but crystalline. 6.5 mils removed. 1.81 g removed. Good line definition.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations			Interpretation of Results	Conclusions and Recommendations
				Time	I	E		
M-91	To ascertain the effect of AC on M-90, Run No.3.	Same As M-90.	Same setup with AC circuit consisting of two capacitors, 4000μF and 3000μF in series. AC voltage set at 4 v.	0	2.00	2.51	Gel used was 7 days old.	AC has no pronounced effect.
				3	1.58	3.68		
				5	1.30	4.55		
				11	0.53	7.00		
				30	0.34	7.60		
				51	0.23	7.80		
				60	0.21	8.00		
				82	0.18	8.10		
				103	0.15	8.20		
				121	0.14	8.20		
				142	0.14	8.20		
				180	0.13	8.30		
				4 mils removed. 0.75 g removed. Surface smooth, not crystalline.				
M-92 Run No.1	To ascertain the effect of ultrasonic vibrations on M-90 gel.	Same as M-90.	Acoustica Model DR 50 AH was used as vibrational source A thin brasing rod held in place by springs transferred vibrations from bottom of tank to anode, which was clamped onto bracket extending from rod.	Without vibrations.				Amount of metal removed was unaffected by ultrasonics Resistance of cell, however, was lowered.
				Time	I	E		
				0	0.50	1.60		
				14	0.25	2.09		
				22	0.16	2.26		
				31	0.12	2.31		
				1 mil removed. 0.16 g removed. Surface crystalline.				
Run No.2				Acoustica set at 70 ma.				
				0	0.50	1.50		
				5	0.47	1.40		
				12	0.30	1.80		
				16	0.23	1.90		
				20	0.20	1.96		
				30	0.16	2.02		
				1 mil removed. 0.16 g removed.				

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-93	To ascertain the characteristics of NH_4F as an electrolyte for Inconel X.	100 ml H_2O 20 g NH_4F	Standard liquid electrolysis.	Time / I / E 0 / 0.50 / 2.33 Slight cathodic gassing. 12 / 0.54 / 2.27 Gassing commences at 1.25 v. 30 / 0.56 / 2.19 0.21 g removed. Surface entirely smooth. If NH_4F conc. is increased to 30%, then NH_4F crystallizes on anode.		Etch rate is slow but clean. Electrolyte will be gelled.
M-94	To ascertain the characteristics of NH_4F in a CMC gel on Inconel X	100 ml H_2O 15 g NH_4F 10 g CMC 12 g acetone				Solution would not gel.
M-95	To ascertain the characteristics of a Hi-Sulfate Electrolytic Nickel Bath.	100 ml H_2O 11.25 g $NiSO_4 \cdot 6H_2O$ 9.75 g $NaSO_4$ 3.00 g NH_4Cl 1.50 g H_3BO_3	Standard liquid electrolysis.	Time / I / E 0 / 0.50 / 2.38 Gas bubbles form on cathode. 12 / 0.50 / 2.41 30 / 0.45 / 2.51 0.23 g removed. Etch consists of fine pitting.		No improvement over other commercial nickel baths.
M-96 Run No.1	To rerun M-90 with a thicker gel to ascertain if total etch can be increased on Inconel X.	M-89 70 ml H_2O 30 ml HF 25 g $NiCl_2 \cdot 6H_2O$ 3.5 g Na_2SO_4 11.0 g CMC 12 ml acetone	One inch thick gel. Honeycomb underneath, Inconel anode on top.	Time / I / E 0 / 1.30 / 2.35 5 / 1.36 / 2.27 13 / 0.92 / 3.51 33 / 0.51 / 4.81 68 / 0.32 / 5.50 100 / 0.24 / 5.70 121 / 0.22 / 5.80 136 / 0.21 / 5.83 160 / 0.19 / 5.88 180 / 0.18 / 5.88 Line definition beginning to be lost.	Line delineation seems to be lost due to crystallization within gel.	An increase in gel thickness does not result in a commensurate increase in total etch.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-96 (con.) Run No.2			Same as Run No.1.	Time / I / E 0 / 0.37 / 5.25 35 hrs / 0.07 / 6.00 3.22 g removed. 9.5 mils removed. No line delineation left. Gel crystallized and spread out over entire anodic surface. Etch rough in texture but even throughout.		
M-97 Run No.1	To ascertain if etch rate can be increased if gel M-90 is immersed in electrolyte.	Same as M-90.	1/2-inch gel immersed in 3/8-inch of electrolyte M-89. A S.S. honeycomb is placed along side gel in petri dish.	Time / I / E 0 / 1.00 / 2.89 15 / 0.64 / 3.73 50 / 0.34 / 4.70 85 / 0.27 / 5.20 120 / 0.22 / 5.29 150 / 0.21 / 5.29 180 / 0.20 / 5.38 3 mils removed. Poor line delineation.		No improvement in etch rate is seen. Crystallization in exposed portion of gel seems to be the cause.
Run No. 2			3/4-inch gel in 5/8-inch electrolyte.	Time / I / E 0 / 1.15 / 2.51 1-1/3hrs / 0.28 / 5.38 19-1/2hrs / 0.15 / 9.10 9.5 mils removed. No line delineation.		
M-98 Run No.1	To investigate the previous procedures using a rigid sand casting as shaping tool for Inconel X.	Electrolyte M-89.	100 g 20-30 mesh Ottawa sand, 10 ml sodium silicate. Casting is 3/4-inch thick. 1/2" x 3" 5/8" electrolyte in petri dish. Honeycomb cathode along side.	Time / I / E 0 / 0.95 / 6.10 5 / 1.00 / 5.89 30 / 1.15 / 5.53 Surface etch uneven, line definition very good. 1-2 mils removed, sand casting deteriorates.		Sand casting does not hold up in HF electrolyte. System shows promise however.
Run No.2			Same as Run No.1.	Time / I / E 0 / 0.64 / 6.00 12-1/2hrs / 0.20 / 7.00 Etch deep but very mottled, sand casting eaten away in large sections. Electrolyte crystallized at anodic interface.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-99	To ascertain effectiveness of standard CA gel as shaping tool immersed in electrolyte M-89 on Inconel X.	Standard CA gel. 120 ml $3\underline{N}\ H^+$ $1\ \underline{N}\ NO_3^-$ 36 g CA	1/2" x 1/2" x 3" gel in electrolyte. Honeycomb cathode along side.	Time I E 0 1.00 3.16 5 0.88 3.52 17 0.64 4.18 180 0.18 5.60 Etch mottled and very uneven. Line definition not good.		System not as good as sand casting.
M-100 Run No.1	To ascertain the etching characteristics of DAC Acid No. 8 with sand casting on 321 Stainless Steel.	DAC No. 8. Refer to M-46, Run No. 4.	3/4" x 1/2" x 3" sand casting immersed in 1/2-inch electrolyte. Stainless steel coupon as cathode.	Time I E 0 1.00 2.79 10 0.98 2.83 Etchant begins to break down and attack cathode. Temperature = 144°F. 30 0.59 3.39 Sand casting crumbles to the touch. Etch very mottled, but line definition remains very good. 10 mils removed at deepest etch. 12 mils removed from both sides of cathode.	Etchant too strong in Run No. 1.	Run No. 1 results in too fast an etch rate and mottled surface. Run No.2 much slower with smoother etch. Best results to date.
Run No.2		150 ml DAC No. 8 75 ml H_2O (Results:) 1.33 $\underline{N}$ HCl 1.33 $\underline{N}$ HNO_3 0.67 $\underline{N}$ H_3PO_4 0.27 $\underline{N}$ $FeCl_3$		Time I E 0 0.90 3.29 18 0.90 3.30 39 0.92 3.28 65 0.92 3.29 120 0.91 3.30 Acid replaced with moving sand casting or electrodes 120 0.95 3.15 180 0.98 3.15 195 0.98 3.13 Acid replaced 200 0.98 3.17 230 0.98 3.11 255 0.98 3.10 No black insolubles on sand casting. Etch very uniform compared to Run No.1. Only 3.5 mils removed from center, > 10 mils from valley near edge. Cathode has been attacked to a slight degree.		No polarization effects.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-101	To ascertain the effectiveness of Standard 6-2 Acid with sand casting on stainless steel.	6 $\underline{N}$ H^+ 2 $\underline{N}$ NO_3^-	Same as M-100.	Time I E 0 1.00 3.98 21 1.05 3.72 Cathode begins to be attacked, cut back to: 21 0.20 0.60 13-1/2hrs 0.03 0.90 Electrical connection to cathode had been eaten away. Anode severely pitted with many large, deep pits.		6-2 Acid is too strong, results in chemical attack when bath becomes slightly heated due to electrolysis.
M-102 Run No.1	To ascertain if 3-1 Acid with sand casting results in a satisfactory etch rate and stable electrolyte.	3 $\underline{N}$ H^+ 1 $\underline{N}$ NO_3^-	Same as M-100.	Time I E 0 0.88 2.81 15 0.84 2.89 50 0.72 3.18 72 0.70 3.22 120 0.69 3.28 Very good line definition, etch very mottled, 10 mils at deepest measurement. Black insoluble reaction products clog sand casting. 24hrs 0.04 2.11 Still only 10 mils removed.	Drop in current no doubt due to black insoluble reaction products.	Experiment shows that after 2 hours electrolyte is used up. Not as effective as M-101.
Run No.2			Same as Run No.1. Replace etchant when etch rate begins to fall.	Time I E 0 0.96 2.93 4 0.89 3.13 11 0.88 3.19 20 0.90 3.15 55 0.76 3.51 Acid breaking down, honeycomb cathode being attacked, etchant replaced. 55 0.97 2.87 62 0.88 3.13 81 0.86 3.19 108 0.86 3.19 Etchant replaced.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-102 Run No.2 (con.)				Time / I / E 108 / 0.85 / 3.23 120 / 0.84 / 3.25 130 / 0.84 / 3.26 Line delineation very good, etch mottled, 10 mils at deepest section.		
M-103 Run No.1	To ascertain the characteristics of a 6-2 CA gel as shaping tool immersed in 3-1 Acid on 302 stainless steel.	120 ml 6-2 Acid 36 g CA	1/2-inch gel immersed in 3/8-inch electrolyte. Solid S.S. cathode and 302 S.S. anode. Gel is 8 days old.	Time / I / E 0 / 0.60 / 1.00 20 / 0.50 / 1.18 Black reaction products streaming down sides of gel. Intermittent gassing at anode. 42 / 0.17 / 1.69 64 / 0.20 / 1.63 92 / 0.20 / 1.66 92 / 0.40 / 1.89 125 / 0.39 / 1.90 Surface of gel covered with black layer; seems to be partially soluble. Etch fairly uniform with minor imperfections. 1.5 mils removed.		Etch rate approx. 1/7 of similar etchant in sand casting. Surface more uniform.
Run No.2			Same as Run No. 1 with 16-day old gel.	Time / I / E 0 / 0.42 / 0.71 15 / 0.40 / 0.78 27 / 0.35 / 0.81 60 / 0.30 / 0.84 60 / 0.50 / 1.20 80 / 0.18 / 1.80 85 / 0.40 / 2.03 Current raised. 110 / 0.39 / 2.10 136 / 0.36 / 2.14 170 / 0.36 / 2.14 180 / 0.36 / 2.14 Very good line delineation. Etch uneven, deep valley along edges > 3 or 5 mils. Only 1 mil at shallowest etch. When gel was left in etchant, gas bubbles were seen to emanate from gel.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-104	To ascertain the effect of adding HF to 3-1 etchant with sand casting and 302 stainless steel.	20% HCl = 2 N 8% HNO_3 = 1 N 17% of 30% HF = 12 N	Same as M-100.	Time — I — E 0 — 0.97 — 2.10 11 — 0.95 — 2.29 Sand casting begins to fall apart. 25 — 0.98 — 2.19 Etchant begins to break down, replaced. 25 — 0.99 — 2.17 40 — 1.00 — 2.14 50 — >1.00 — 1.99 Etch rate not noticeably improved, however, polarization is overcome.	Acid still too strong.	HF improves etchant because it stops polarization. An inert shaping tool will have to be found.
M-105 Run No.1	To ascertain the effectiveness of etchant M-104 with 6-2 CA gel.	M-104 Standard CA gel.	Same as M-100. Gel is 6 days old. Honeycomb cathode.	Time — I — E 0 — 0.95 — 1.71 8 — 0.94 — 1.59 50 — 0.89 — 1.61 85 Acid broke down, honeycomb cathode disappeared, electrolyte replaced. 85 — 0.89 — 1.75 100 — 0.88 — 1.77 Cathode beginning to be attacked. Surface uneven with deep cutting confined to edges. Line delineation good. Gel above liquid level impregnated with black reaction products.		Not as effective as M-100.
Run No.2			Lower current density, solid S.S. cathode.	Time — I — E 0 — 0.44 — 0.98 18 — 0.43 — 1.01 37 — 0.39 — 1.11 60 — 0.37 — 1.12 120 — 0.36 — 1.17 Bath has not broken down. Replaced anyway. 120 — 0.38 — 1.11 143 — 0.38 — 1.11 180 — 0.38 — 1.11 190 — 0.40 — 1.10 256 — 0.40 — 1.05 Etch was uneven, some deep valleys near edge. Many uneven portions in center. Gas escapes from gel.		

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-106	To ascertain the effectiveness of a diluted version of etchant M-54 with CA gel as shaping tool for 302 stainless steel.	Standard 3-1 Acid CA gel electrolyte: 50% H_2O 6% H_2SO_4 27% H_3PO_4 6% HCl 3% HNO_3 8% HF	Same as M-10 Gel 6 days old.	Time I E 0 0.48 0.88 15 0.38 1.01 38 0.35 1.11 60 0.31 1.19 90 0.26 1.29 Bath light green. Replaced. 90 0.29 1.22 Current raised. 90 0.50 1.49 180 0.20 2.12 No improvement.		No improvement over M-105.
M-107 Run No.1	To investigate a new etchant for Inconel X.	(Original) 81 g/l Fe 17 g/l Cr 3.4-3.8 $\underline{M}$ NO_3^- 3.8-4.2 $\underline{M}$ H^+ 0.5-1.0 $\underline{M}$ PO_4^{--} (Actual) 392 g/l $FeCl_3 \cdot 6H_2O$ = 81 g/l Fe 276 ml HNO_3 36 ml H_3PO_4 688 ml H_2O	A rigid shaping tool made from 20-30 mesh Ottawa sand was immersed in etchant 3/16 inch from top. A Pt. gauze cathode was placed in reservoir beside porous tool.	Time I E 0 2.00 7.45 No cathodic gassing, slight anodic gassing. 6 1.78 7.75 26 1.15 8.05 60 0.74 8.25 79 0.57 8.45 120 0.36 8.60 Electrolyte replaced. 120 0.75 8.28 188 0.83 8.05 Etch mottled and uneven. 23 mils at deepest point, 3 mils at shallowest. Line delineation was good.		No further study is immediately planned for this electrolyte.
Run No.2	To rerun for longer time at a lower current density.			Time I E 0 0.50 2.54 No electrode gassing. 14-1/2hrs 0.21 2.40 Etch has same characteristics as Run No. 1, 30 mils at deepest, 3 mils at shallowest. For both runs, the porous tool seemed slightly plugged.		

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-108 Run No.1	To investigate a new etchant for Inconel X.	36% v H_2O 20% H_2SO_4 10% HNO_3 6% HCl 28% $FeCl_3 \cdot 6H_2O$ Sp. Gr $FeCl_3 \cdot 6H_2O$ = 1.63 g/ml	Sand casting made with 50-70 mesh Ottawa sand immersed in etchant. A Pt. cathode was used.	Time I E 0 0.63 4.09 10 0.11 4.51 25 0.06 4.55 60 0.04 4.50 1 mil removed, surface mottled.		Resistance is disappropriately high, polarization severe. No further work planned.
Run No. 2			Same potentiometric setting with coarser sand casting (20-30 mesh).	Time I E 0 0.54 4.17 13 0.16 4.50 27 0.12 4.52 60 0.08 4.52 No improvement over Run No. 1.		
M-109	To reevaluate M-100 using Pt. cathode.	DAC Acid No. 8.	20-30 mesh Ottawa sand casting Pt. gauge cathode alongside of porous shaping tool.	Time I E 0 0.77 3.50 20 0.67 3.50 30 0.76 3.45 60 0.99 3.32 130 0.98 3.26 180 0.92 3.32 3 mils removed.	No change in circuit was made. Conductivity of electrolyte must be increased as reaction products enter etchant.	The results are not in agreement with those of M-100, Run No.1. Temperature rise, if any, was not looked for. This may account for discrepancy. Further correlation studies will be conducted.
M-110	To ascertain the effectiveness of employing a hallow procelain candle as a shaping tool with DAC Acid No. 8 on 302 stainless steel.	DAC Acid No. 8.	A 1/2-inch dia. cylindrical candle was immersed in a reservoir of DAC No. 8 to within 3/16 inch from top. A Pt. cathode was used.	Time I E 0 1.40 3.59 1 hr 1.25 3.85 13-1/2hr 0.06 4.80 Cut has successive ridges and two high spots. Line definition good. 45 mils removed in center of hemispherical cut.		This technique shows promise. Will be studied at a later date.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-111	To investigate a new S.S. etchant as a straight liquid.	2.5 M NO_3^- 4.5 N H^+ 68.7 g/l of 17-7 stainless steel	Etchant was placed in a two-compartment neoprene cell with liquid level in cathode side higher than anode side. Anode was placed horizontally on top of etchant. Anode compartment was fitted with air vent. A Pt. cathode was employed.	Time I E 0 1.50 2.5 3 hrs 1.47 2.5 Excellent line definition, etch smooth over two-thirds of area away from gas vent. 67 mils removed from two-thirds, 47 mils removed from one-third near vent.	Neoprene cell enables etchants to be evaluated in liquid form while keeping H_2 gas completely away from anode. Gassing is caused by gas precipitation due to decreased solubility when acid contains metallic ions. Gassing can also be due to boiling when current density is too high.	This is an excellent liquid etchant but requires many hours to balance. It is desired to work with simpler etchants.
M-112	To compare DAC Acid No. 8 with M-111 in neoprene cell.	DAC Acid No. 8.	Same as M-111 except vent was provided with a small vacuum line to remove foam.	Time I E 0 1.60 2.5 90 1.55 2.5 Surface very good. Shiny and smooth except for one long area near edge that was affected by vacuum line in vent. 34 mils removed.	Very good results are obtained from neoprene cell.	M-111 is a better etchant, but DAC No. 8 is still satisfactory.
M-113	To compare a HCl - HF etchant to DAC No. 8 in neoprene cell.	6 N HCl 3 N HF	Same as M-111 except vent was plugged.	Time I E 0 2.40 2.50 Cut back to: 0 1.00 1.22 225 0.98 1.24 Anode was covered with heavy black layer. 33 mils removed in center, 4 mils at vent, 28 mils at other end. Gas was entrapped in vent end of compartment. Surface even but crystalline.	Conductivity is improved over all previous etchants. HF must have been exhausted, thus permitting black layer to form.	At present, not as satisfactory as DAC No. 8.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-114 Run No. 1	To ascertain the effectiveness of employing a porous Carborundum block as a shaping tool when immersed in DAC No. 8.	DAC Acid No. 8.	A 1/2-inch thick piece of Carborundum filtering disk was immersed in usual manner. Porosity No. 50 obtained from "Carborundum Co." (highest porosity available). Anode was placed directly on top of shaping tool.	Current maintained @ 1 a, no other readings taken. After 3 hours surface was irregular with high and low spots corresponding to roughness of shaping tool. 21 mils removed in low spots, 13 mils in high spots.	Good conductivity can be maintained. This shows that pores do not plug appreciably.	Initial studies show that considerable metal can be removed. Surface texture is not good. Further work will be done to improve this. Removing the anode from shaping tool surface does not improve overall etch.
Run No. 2			5-mil shims were placed between tool and anode.	After 3 hours @ 1 a, there was a deep channel cut around perimeter with little cutting in center. 30 mils near perimiter, 4 mils in center.		
Run No. 3			Anode lifted 5 mils from shaping tool by neoprene supports.	Exactly the same results as Run No. 2.		
M-115 Run No. 1	To ascertain the effectiveness of employing a porous alumina disk as a shaping tool with DAC Acid No. 8 on stainless steel.	DAC Acid No. 8.	A 1-5/8-inch dia., 1/8-inch thick Alumina Disk No. 393 obtained from American Lava Corp. Porosity approx. 18% water. Disk was placed on three plastic props. Acid added to petri dish until meniscus reaches bottom of disk. Anode placed directly on top.	Time / I / E: 0 / 1.60 / 2.888 4 / 0.85 / 3.32 11 / 0.52 / 3.62 43 / 0.32 / 3.72 76 / 0.34 / 3.71 120 / 0.18 / 3.81 3 mils removed. Surface uniform and shiny. Alumina disk is plugged with reaction products.		Porous disk hinders flow of reaction products thereby making system unworkable in present phase.
Run No. 2			Start at a lower current density.	Time / I / E: 0 / 0.90 / 2.20 5 / 0.50 / 2.48 12 / 0.45 / 2.49 Increase to: 12 / 0.71 / 3.50 40 / 0.32 / 4.00 70 / 0.30 / 4.00		

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-115 Run No.2 (con.)				Time / I / E 110 / 0.28 / 3.98 133 / 0.32 / 3.87 173 / 0.59 / 3.72 212 / 0.99 / 3.42 220 / 1.00 / 3.40 5 mils removed near edges, 3-1/2 mils in center. Surface shiny and smooth.		
Run No.3				Time / I / E 0 / 2.00 / 2.71 16.5 hrs / 0.40 / 3.98 23 mils near edge, 8 mils in center. Surface severely mottled.		
M-116	To try an HCl-HF etchant with alumina shaping tool of M-115 in hopes that reaction products will be rendered more diffusable.	6 N HCl 3 N HF	Same as M-115.	Time / I / E 0 / 0.92 / 1.02 3 / 0.26 / 1.40 Increased to: 3 / 0.57 / 2.93 8 / 0.64 / 2.89 20 / 0.60 / 2.90 42 / 0.45 / 2.98 60 / 0.42 / 2.95 A green gelatinous mass accumulated at anode-tool interface. No etch in center. Deep channeling near edge.		Etchant not as effective as DAC No. 8.
M-117 Run No.1	To determine the relationship between pore size of Carborundum shaping tools and resulting etch.	DAC No. 8.	Three porosity grades, Nos. 50, 30, 20, were placed in etchant side by side. Anode was placed directly on top.	Time / I / E 0 / 1.00 / 1.85 20 / 1.15 / 1.79 60 / 1.20 / 1.80 All three etches show mottled surfaces. Nos. 30 and 20 show a more uniform etch than No. 50. Less channeling near edge, smaller radius to mottling.		More metal can be removed with a coarser shaping tool. Serious defects result, however, in channeling near edges of etch.

APPENDIX D (Continued)

Expt No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-117 (con.) Run No. 2				Time / I / E 0 / 1.40 / 1.70 Same circuit as Run No. 1. 60 / 1.10 / 1.87 Acid replaced. 60 / 1.00 / 1.91 120 / 1.15 / 1.81 Acid replaced. 120 / 1.00 / 1.91 140 / 1.10 / 1.78 180 / 1.05 / 1.84 Difference between numbers 20, 30 and 50 is more pronouaced. Channeling in 50 is further advanced, except for this, however, there seems to be little increase in metal removal over Run No. 1 @ 1 hour.		The decrease in the etch rate in Run 1 and No. 2 can only be attributed to the plugging up of the shaping tool with reaction products. It is recommended that a flow process be initiated through the shaping tool, these by washing out there reaction products. A major problem will be line delination. Further work is planned on this aspect.
M-118	To ascertain the effect of applying mechanical vibrations to anode on top of Carborundum shaping tool.	DAC No. 8	No. 30 Carborundum with anode on top. A vibratool was clamped above anode. A flat-end, case hardeand 7/32-inch drill stock transmitted the vibrations	Time / I / E 0 / 1.20 / 2.12 19 / 0.78 / 2.36 80 / 0.57 / 2.50 Etch improved over same condition without vibrations.	The flow encountered in Run No. 3 occurred because anode was on a slight angle, the vibrations induced the subsequent flow of acid through the shaping tool and along underside of anode.	Run No. 1 and 2 show improvement with vibrations. Run No. 3 shows that a slight flow rate either induced by vibrations or pumping will enhance etch by rendering it uniform. Further work will be done on induced flow rates, with or without vibrations. The coarser tool (No. 50) seems to be better for all purposes.

APPENDIX D (Continued)

Expt No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-118 Run No. 2			No. 50 Carborundum	Time I E 0 0.86 2.08 3 1.00 2.00 10 1.00 2.02 15 Vibrations were turned off to facilitate adjustments for several seconds, when turned on again: 15 0.82 2.12 20 0.82 2.12 86 0.69 2.21 Acid replaced. 92 0.82 2.11 144 0.99 1.99 Acid replaced. 150 0.70 2.26 180 0.64 2.29 33 mils at deepest point near edge, 6 mils in center		
Run No. 3			Same set-up, except with 1 x 4-inch anode with two pt. cathode on either side	Time I E 0 1.00 2.00 15 0.96 2.02 45 1.40 1.90 60 0.76 2.27 Acid replaced. 84 0.90 2.18 120 0.74 2.21 Note - 150 ml of acid leaked out of petri dish by being vibrated along the underside of anode which over hanged the side of the dish, surface was mottled, but uniform over entire surface ~35 mils removed.		
Run No. 4			No. 20 carborundum with 4 x 1 anode and 2 pt. cathodes.	Time I E 0 1.05 1.48 7 0.79 1.52 40 0.72 1.59 60 0.70 1.59 Acid replaced.		

APPENDIX D (Continued)

Expt No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-118 Run No. 4 (con.)				Time I E 60 0.69 1.60 68 0.72 1.60 83 0.68 1.60 120 0.56 1.70 Acid replaced. 120 0.74 1.69 125 0.78 1.58 130 0.84 1.52 143 0.80 1.55 180 0.80 1.57 Etch was confined to perimeter, approximately 30 mils, 3 mils in center. Roughness in center less than No. 50 Carborundum.		
M-119	To induce a flow rate through a Carborundum shaping tool from bottom to top.	DAC acid No. 8	A 3/8-inch dia. hole was drilled 5/16 inch through a 1/2 inch thick No. 50 Carborundum block. A glass "U" tube was inserted in bottom and held in place by DAC steel maskant. All but top face of Carborundum was immersed in this maskant. Acid is fed into other end of "U" tube at desired flow rate. The burgess vibra-tool was setup above anode in previous manner. A pt. cathode was laid next to shaping tool. A lin. liquid head was maintained in feed tube. A vacuum line remover acid over flow from petri dish. Acid level was maintained within 3/16 inch from top of shaping tool.	Time I E 0 0.47 3.19 10 0.44 3.12 60 0.46 2.97 120 0.48 2.99 180 0.60 2.89 Etch was covered with a black ppt. Etch was confined to perimeter, 60 mils with 8 mils in center. Etch was crystalline in texture	It is felt that deep perimeter etching is caused by the greater degree of acid freedom near perimeter.	Spent acid was not recycled at this time, if H^+ ion were determined, acid could be rebalanced and recyeled. Etch rate not satisfactory. Further work is planned on this system.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-120	To ascertain if etch characteristics of M-119 can be improved by raising anode from shaping tool.	DAC acid No. 8	Same as M-119 except pt. (1 x 5 inch) cathode was placed underneath carborundum shaping tool. Anode supported on three neoprene supports which lifted anode approximately 10 mils from Carborundum surface.	Time / I / E 0 / 0.84 / 3.00 5 / 0.64 / 3.15 13 / 0.66 / 3.13 50 / 1,000 ml of spent acid recycled. 60 / 0.78 -0.85 / 2.92 100 / 1,000 ml recycled 120 / 0.58 -0.62 / 3.09 180 / 0.38 / 3.28 Etch smooth, but only 3 mils deep in center. 25 mils near two edges where cathode extends underneath the Carborundum block.	Fluctuations of current probably due to gassing at anodic interface.	Further work is planned with different cathode configurations.
M-121	To investigate the effectiveness of putting holes through alumina disk of M-115 and etching in same manner.	DAC acid No. 8	1/32 inch dia. holes 3/16 inch between centers. Setup same as M-115.	Time / I / E 0 / 2.00 / 2.11 Cathode moved 3 inches from anode to avoid copious gassing. 0 / 1.45 / 2.36 7 / 0.81 / 2.69 Cathode moved back to 1/2 inch from anode. 7 / 0.91 / 2.60 44 / 0.46 / 2.82 60 / 0.44 / 2.86 Etch uniform, smooth but only 2 mils.		Reaction products plug holes as well as pores. Further work will be done on vibration and hydrostatic heads.
M-122	To ascertain the effect of mechanical vibrations on anode of M-121.	DAC acid No. 8	Same as M-121 with vibra-tool	Time / I / E 0 / 1.20 / 0.62 10 / 1.05 / 0.72 20 / 0.86 / 0.77 21 / 0.78 / 0.82 22 / 0.73 / 0.84	The decrease in resistance can not be fully explained. It is doubtful if this is due entirely to the vibrations.	Vibrations help etch rate somewhat, but not sufficiently.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-122 (con.)				Time I E 26 0.50 0.96 32 0.34 1.06 44 0.20 1.11 Vibrations increased to a point just below splashing of reservior. 44 0.55 0.92 60 0.60 0.90 Vibrator off. 65 0.86 0.76 Vibrator on. 65 0.86 0.76 66 0.65 0.88 2 mils removed overall, with 3 mils were holes had been.		
M-123	To ascertain if a small hydrostatic head under alumina disk with holes will enable a more uniform and faster etch rate to be developed.	DAC acid No. 8	Insert alumina disk in one end of a flex hose from an automobile radiator, bend tube into "U" shape and drip acid into other end. Insert Pt at bend. Place Anode directionly on top of disk and apply vibra-tool.	Time I E 0 0.49 2.44 30 0.46 2.38 Gas becomes entrapped under anode. I 0 when this occurs.		Anode will have to be raised above disk to allow gasses to escape.
M-124	Rerun M-122 with disk containing 10 times the number of holes.	DAC acid No. 8	Same as M-122	Time I E 0 2.30 0.40 50 2.00 0.58 Etch not satisfactory, only 1.5 mils and not uniform.		Decreasing the mass of alumina decreases electrical resistance substantially, will use this disk for subsequent work.

APPENDIX D (Continued)

Expt. No.	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-125	Rerun M-124 with anode 1/16 inch above disk.	DAC acid No. 8	Anode was held above disk by 3 Ni-Chrome wires inserted in rubber tube. No vibrations.	Time / I / E Flow rate 10.1 ml/min. 0 / 0.62 / 2.92 26 / 0.65 / 2.84 60 / 0.66 / 2.81 Etch rate smooth and uniform, only 2 mils. 25.2 ml/min 0 / 0.50 / 3.15 75 / 0.51 / 2.90 1,000 ml acid recycled. 140 / 0.52 / 2.99 1,000 ml fresh acid added to reserior. 240 / 0.50 / 2.95 1,500 ml acid recycled. 6 hrs. / 0.50 / 2.98 line delineation very good etch has several high spots 15-9 mils removed.		Procedure demonstrates that metal can be removed. Any shaped tool can be utilized where in acid is slowly forced through shaping tool. Etch rate still not satisfactory.
M-126	Rerun M-125 with $HCl-HNO_3$ etchant.	Standard 3:1 $HCl-HNO_3$	Same as M-125	Time / I / E Flow rate 32 ml/min. 0 / 0.62 / 3.02 25 / 0.70 / 2.82 Considerable anodic gassing. 4 hrs. / 0.68 / 2.71 Surface is very rough 40-55 mils removed across an area 1-1/2 inches in dia. Next 1/4 in. has sloping sides.	Stoping sides due to gassing and high flow rate.	Further work will be done.
M-127	Rerun M-125 with more concentrated $HCl-HNO_3$ etchant.	6-2 $HCl-HNO_3$	Same as M-125 except no restriction will be placed on cell voltage. Electrolyte seems to gas at anode in any event.	Time / I / E Flow rate 20 ml/min. 0 / 3.20 / 12.0 5 / 3.55 / 11.8 200 Etch came through anode. 120 mils, not uniform, 70 mils in some spots, surface rough. Considerable gassing, line definition not bad but sloping occurs.	A good portion of anodic gassing was due to boiling of etchant.	Concentrated acids at higher current densities produce faster etch rates, but unsatisfactory etches. Further work will be done.

APPENDIX D (Continued)

Expt. No	Purpose	Formulation	Procedures and Test Conditions	Observations	Interpretation of Results	Conclusions and Recommendations
M-128	Rerun previous with DAC No. 8	DAC acid No. 8	Same as M-125 and 127	Time I E Flow rate : 5.5 ml/min. 0 2.60 12.2 35 Etchant begins to boil and flow rate is insufficient to maintain overall liquid contact with anode, increased to 23 ml/min. 160 2.80 12.4 Etch not smooth, bur more uniform than 126 or 127. 50-65 mils with a 1/8 inch ring where etch slopes to original surface.		Run No. 2 shows best etch to date. Will continue work on this system.
Run No. 2				Time I E 0 2.50 12.2 180 2.40 12.1 Etch shiny and smooth and uniform over 1/2 of area. Remainder has several high spots due to gas entrapment caused by anode coming to close to alumina where a supporting prong gave away. Line definition not satisfactory, slopes.		

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Electrical current applied to the gel etchant increases the etch rate and reduces gaseous reaction products.
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